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EXPERIMENTAL PROOFS

OF

CHEMICAL THEORY.

EXPERIMENTAL PROOFS

OF

CHEMICAL THEORY

FOR BEGINNERS.

BY

WILLIAM RAMSAY, PH. D.,
PROFESSOR OF CHEMISTRY IN UNIVERSITY COLLEGE, BRISTOL.

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PREFACE.

THE experiments described in this little book have formed the preliminary work of all students beginning chemistry in my laboratory for the last two years. I am convinced that such a course has the advantages of familiarizing the student with the subjects treated in the first term of an ordinary course of lectures; of giving him practice in the construction of apparatus; and of making him perform calculations with a definite object, instead of as merely theoretical problems.

I have not found any difficulty in getting students to construct their own apparatus; after a few preliminary lessons in cork-boring, bending glass tubes, etc., the demonstrator is put to little trouble; and it is easier to start a number of students in this manner than in the usual course preliminary to qualitative analysis. I have found that after such a course as this, it is easy for a student of ordinary intelligence to acquire a knowledge of qualitative analysis; and it is noteworthy that the detection of unknown substances is accomplished much more rapidly and accurately after such preliminary training.

The accuracy of the results obtained by these comparatively rough methods is surprising; the density of gases is found usually within three or four per cent. of the truth; and results of analysis seldom show an error of one per cent. Of course good results are obtained only by careful workers, and I make it a rule that each experiment shall be repeated until a satisfactory result is obtained. The whole course occupies a term of ten weeks, the student working three whole days a week.

Chapter VII. must be read repeatedly until the ideas it contains are thoroughly assimilated; but it need not delay the student in prosecuting the experimental part of his work.

In order to complete the subject, the Periodic Law has been treated of in Chapter XII. This demands a knowledge of compounds of the metals greater than a beginner can have; it is better therefore to postpone it until the lecture course has been finished. It appeared to me advisable to consider this subject, as by means of the Periodic Law many atomic weights have been corrected and several new ones discovered; and a book like the present would not have been complete without some such sketch.

I have no doubt that many of the processes herein described are capable of improvement and that better processes may be devised by those who use this book; the methods here described are merely the best which have occurred to me for giving a general knowledge of the principles of chemistry.

Having learned by experience the benefit of a systematic experimental study of the elementary facts which serve as the basis of chemistry, I venture to recommend this plan of teaching to others, in the hope that it may receive a trial, and prove equally satisfactory in their hands.

N.B. The student is recommended to provide himself with a Table of Logarithms.

UNIVERSITY COLLEGE, BRISTOL.
January, 1884.

APPENDIX TO PREFACE.

As some chemists to whom I have mentioned the various processes described in the following pages have been curious to know the degree of accuracy of the results which the methods are capable of yielding, I append some of those obtained by two of my last year's students, both of whom were fairly good workers, and neither of whom had previously practised manipulation.

	A.	B.	Standard Numbers.
Weight of a litre of air	1·290 gram	1·301	1·296
,, ,, oxygen	1·431 ,,	1·422	1·433
,, ,, nitrogen	1·241 ,,	1·242	1·255
,, ,, ammonia	0·764 ,,	0·758	0·761
,, ,, chlorine	3·151 ,,	3·180	3·171
,, ,, hydrogen chloride	1·620 ,,	1·638	1·630
,, ,, carbonic anhydride	1·931 ,,	1·953	1·971
Composition of air by weight O	22·98 p.c.	22·97 p.c.	23·14
,, ,, N	77·01 ,,	77·03 ,,	76·86
Analysis of ammonia N	82·4 ,,	81·9 ,,	82·35
,, ,,	17·6 ,,	18·1 ,,	17·65
Coefficient of expansion of air	0·00358 *t*	0·00362 *t*	0·003665
Relation, $PV_1 = P_1V$	2358 : 2384	1234 : 1276	
Equivalents of Aluminium	8·72	8·85	9·0
,, Zinc	31·64	31·31	32·45
,, Tin	59·03	58·62	58 85

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CHEMICAL THEORY.

CHAPTER I.

MEASUREMENT OF TEMPERATURE, PRESSURE, AND WEIGHT.

§ 1. THE fundamental principles of chemistry rest on experimental proof; and it is the object of the following pages to give such instruction to those beginning the science, that they may demonstrate with fair approximation to accuracy, the truth of these principles. In so doing, it is necessary to make measurements of *volume*, and of *weight.* The volume of any substance, whether solid, liquid, or gaseous, is not a constant quantity, but depends on the temperature and pressure at which it is measured. It is therefore necessary first to consider the methods of measuring temperature and pressure.

§ 2. *Measurement of temperature.*—Temperature is usually measured by means of the expansion of mercury in a thermometer. Although this plan has certain disadvantages, yet it surpasses in convenience all other methods. As mercury remains liquid as low as −40°, and does not change to gas until heated to about 360°, a great range of temperature is secured.

Moreover the expansion of mercury is much more nearly equal for equal rise of temperature than that of any other liquid, and as the slight irregularity is nearly counterbalanced by the expansion of the glass of which the thermometer is constructed, the readings of a good mercury thermometer are almost absolutely correct.

The melting-point of ice is practically constant, and is almost uninfluenced by any alteration of the pressure of the atmosphere; it is adopted as the zero-point (0°) of the centigrade thermometer, and it corresponds with 32° on Fahrenheit's scale. The boiling-point of water is a constant temperature, provided the pressure does not vary; at a pressure of 760 millimetres of mercury in the barometer, the boiling-point of water corresponds to the number 100° on the centigrade or hundred-degree scale, and to the number 212° on the Fahrenheit scale. Thermometers graduated on the stem from – 10° to 300° can be procured for 4*s*. or 6*s*.

§ **3.** *To determine the temperature* 100° *of a thermometer.*—The temperature of a liquid when boiling is never constant. The level of the mercury of a liquid will be seen to vary by jumps of sometimes as much as a degree owing to the bubbles of vapour being evolved spasmodically, not regularly, and boiling water, in the intervals of ascent of the bubbles, rises in temperature somewhat above 100°; but as soon as steam escapes freely the temperature again falls to 100°. The temperature of steam rising freely from boiling water, while the barometer registers a pressure of 760 millimetres, remains constant at 100°. The thermometer should therefore be exposed to the steam, but not touch the boiling water.

§ 4. The mercury in the stem of the thermometer expands, as well as that in the bulb; consequently the whole of the portion of the stem containing mercury should be in contact with the steam.

§ 5. The apparatus employed to determine the boiling-point is constructed as follows:—*F* is a flask supported by wire-gauze over a low Fletcher's burner, or if preferred, on the ring of a retort-stand over a Bunsen's burner; the steam from the boiling water in the flask escapes through the tube *B* in which the thermometer *A* hangs, supported by the cork *E*, through which it passes, heating the thermometer to its own temperature; it then passes through the space between *B* and *C*, and finally escapes by the tube *G*. At *D* a piece of wide india-rubber tubing serves as a cork, to join the internal tube with the encasing one *C*; and if necessary, a similar piece of tubing may be used in coupling the tube *B* with the flask. The object of the encasing tube is to protect the inter-

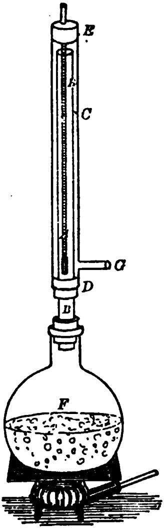

Fig. 1.

nal one from draughts, and to maintain a uniform temperature. The position of the upper surface of the mercury in the thermometer is then read off, tenths of a degree being estimated by eye. It is sometimes rather difficult to read the thermometer accurately, owing to the condensation of drops of water on the glass; these however are easily removed by warming the encasing tube with a spirit-lamp, immediately before reading.

§ 6. It is difficult in reading to avoid "parallax" (an apparent change in the position of an object owing to a change of position of the observer) owing to the eye not being in the same horizontal plane as the mercury; if the eye is too high, the temperature registered will be in excess of the real one; if too low, too low a temperature will be recorded. This difficulty may be overcome to some extent by folding half a sheet of note-paper evenly round the encasing tube, and reading from the lower edges; or perfectly, by using a cathetometer, or reading telescope.

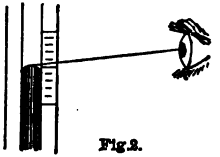
Fig. 2.

§ 7. As the temperature at which a liquid boils depends on the pressure to which it is exposed, it is necessary to read the barometer immediately after determining the boiling-point. The alteration of the boiling-point of water produced by pressure has been

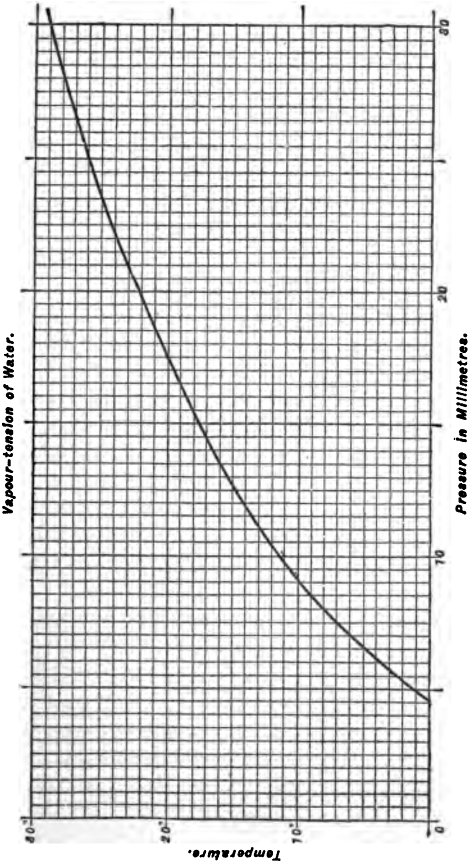
Vapour-tension of Water.

Fig. 3.

carefully investigated, and is represented graphically in the accompanying curve. It may be found approximately by the formula

$$D = 0{\cdot}0375\ (760 - p)$$

in which D is the required correction, and p the pressure of the atmosphere in millimetres.

§ 8. *To determine the zero-point of a thermometer.*—It is found that the glass forming the bulb of a thermometer alters its condition slowly, after it has been filled with mercury. If the thermometer, as is usually the case, has been graduated soon after the bulb has been filled, the zero-division of the scale no longer registers the melting-point of ice; and it is therefore necessary to check the graduations by a fresh determination. For this purpose, some snow, or finely-pounded ice is placed in a beaker, and the thermometer bulb sunk in it until the mercury in the stem is just visible. The position of the mercury in the stem, after some time, is then read off to one-tenth of a degree, attention being paid to parallax (§ 6); and the temperature noted.

§ 9. Having thus ascertained the zero-point and boiling-point of the thermometer, the value of the intermediate divisions may be found by marking these points on curve-paper, as shown on p. 7, and joining them by a straight line. For any given temperature, the length of the ordinate must be added to, or subtracted from the recorded temperature; the result will be approximately accurate.

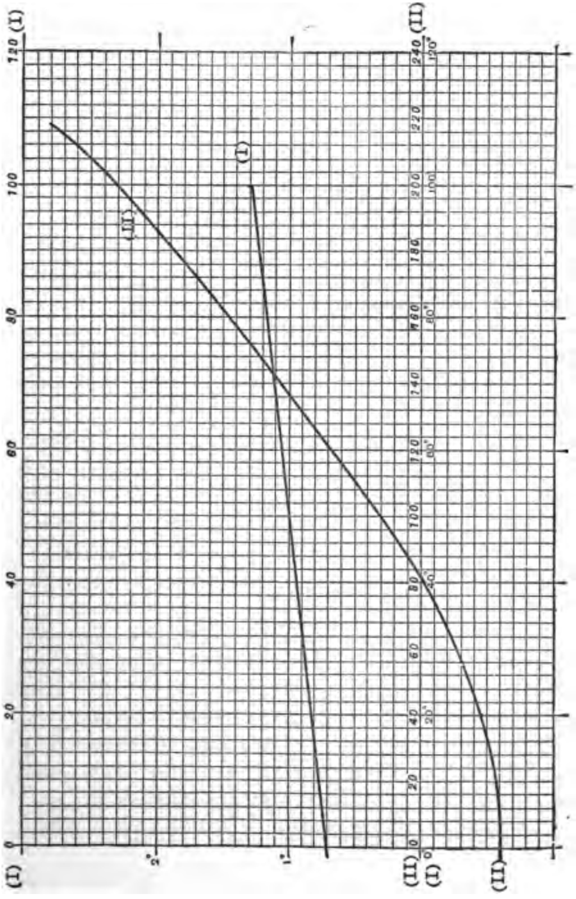
(I)
(II)
(I)
(II)
0
20
40
60
80
100
120 (I)
0
20
40
60
80
100
120
140
160
180
200
220
240 (II)
0°
20°
40°
60°
80°
100°
120°
1°
2°
(I)
(II)

Fig. 4.

§ 10. To ensure closer approximation to accuracy, regard must be paid to the fact that the bore of the thermometer-tube is rarely, if ever uniform, so that the tube is not cylindrical, but conical, or indeed composed of several portions of cones. The simplest method of correcting for this error is as follows:—Invert the thermometer, and tap it. A column of mercury usually separates and falls to the lower end. Note the length of this column; if it is shorter than 50 degrees, place the thermometer again in its normal position, and warm it so as to make the distance between the upper end of the column and the place of junction with the mercury nearly equal to 50 degrees; if longer than 50 degrees, cool the mercury in the bulb with cold water or ice, until the same is the case. Then re-invert it, and tap it. By repeating this process several times, it is possible to separate a column very nearly equal to 50 degrees in length. Place the thermometer in an inclined position, so that the mercury occupies a position from 0° to nearly 50°. By gently tapping one end, it can be made to coincide accurately with the zero-point. Then by means of a lens, read the position of the other end of the mercury. For example suppose it to be at 50·9°. The difference between this number and 50° is +0·9; $\delta_1 = +0{\cdot}9$. Similarly, when one end of the mercury column is at 50°, the other end reaches to 100·4. Here $\delta = +0{\cdot}4$. Again, with one end at 100°, the other is at 150·2; $\delta = +0{\cdot}2$. At 150°, the mercury extends to 200°; $\delta = 0$; and at 200°, the column extends to 249·6, hence

$\delta = -0{\cdot}4$. The zero-point, moreover, was ascertained to be at +0·6°, and 100° at 99·7°. The method of correcting is given as follows :—(a = correction for each 50 degrees).

$$a=\frac{0{\cdot}6+0{\cdot}3+0{\cdot}9+0{\cdot}4}{2}=+1{\cdot}1.$$

The number 0·6 is the zero-point; this number must therefore be added. The number 0·3 is the difference between 99·7 and 100. It must therefore be subtracted; but it is a minus quantity, hence it must here be added; similarly 0·9 is the first difference, δ_1, and 0·4 the second difference, δ_2. These differences both occur in the first hundred degrees. The length of the thread of mercury was 50, $=\frac{100}{2}$; hence to make these corrections apply to every 50 degrees, they must be divided by 2. Tabulating as follows, the true temperatures are ascertained :—

Division							Correction
0		−0·6					= −0·6
50	1·1	−0·6	−0·9				= −0·4
100	2·2	−0·6	−0·9	−0·4			= +0·3
150	3·3	−0·6	−0·9	−0·4	−0·2		= +1·2
200	4·4	−0·6	−0·9	−0·4	−0·2	−0·0	= +2·3
250	5·5	−0·6	−0·9	−0·4	−0·2	−0 + 0·4	= +3·8

(For an explanation of this method see Kohlrausch, *Physical Measurements.*)

Having thus ascertained the errors of the thermometer, it is advisable to plot them on curve-paper for reference, expressing the corrections on a large scale compared with the degrees. This has been done in the diagram on p. 7, with no. II. The correction for intermediate temperatures is thus made easy. For example when 40° is read the correction is −0·47, and the real temperature is 39·53°; at 83, the readings are correct; at 150°, the real temperature is 151·2°, and so on.

§ **11.** It is stated that if the thermometer is heated for a week to the boiling-point of mercury, the zero-point becomes constant, owing to the glass acquiring a permanent set; it is usually advisable, however, after the thermometer has been used for high temperatures, to redetermine the two standard points.

In many cases it happens that the stem of a thermometer cannot be exposed to the same temperature as the bulb. A correction must therefore be made to allow for the want of expansion of the mercury in the stem, and this correction is added to the temperature read. The formula usually given for this *exposure-correction* is $y = 0{\cdot}00016\,(T - t)\,N$. ($T$ = temperature read; t, temperature recorded by a small thermometer the bulb of which is placed in contact with the large thermometer, midway between the meniscus of the mercury in the large thermometer, and the lowest point not exposed to the high temperature; it is supposed to register the mean temperature of the mercury in the stem; N = number of divisions not exposed to the high temperature).

The accompanying table summarizes the results. As it is generally sufficient to know the temperature

Exposure correction of Thermometer.

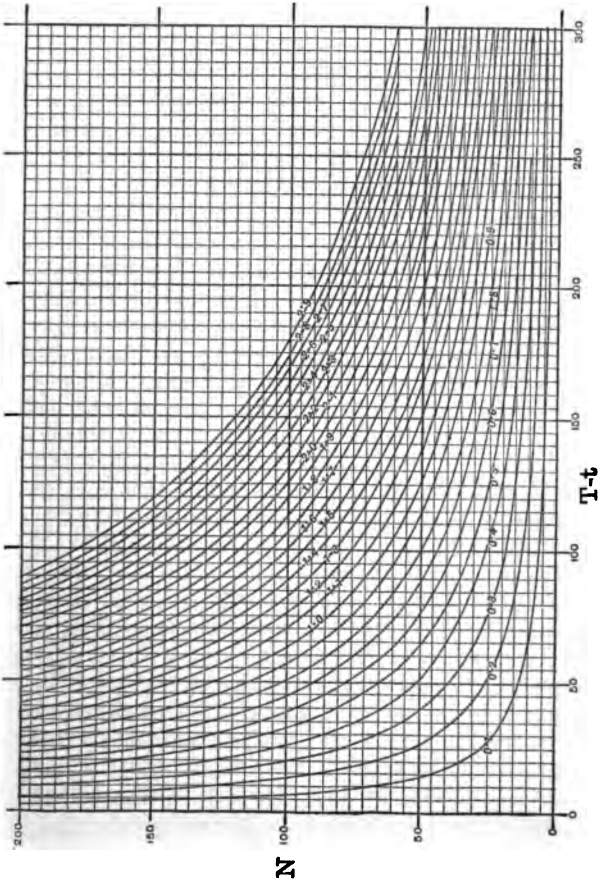

Fig. 5.

to 0·1° the curves have been so constructed as to register that interval. Thus when $T = 180·2$; $t' = 25°$, then $T - t = 155°$, and $N = 90°$, the number of divisions is found by following the line of curve to the right, and the correction is 2·2°. The corrected temperature is therefore $180·2 + 2·2 = 182·4$.

The Fahrenheit scale is often used in this country. As the melting-point of ice is placed opposite the graduation 32°, and the boiling-point of water at 212°, there are $212 - 32 = 180$ divisions between the two points, whereas on the centigrade scale there are 100 divisions. The simplest relations between these numbers are 9 and 5. Hence to convert centigrade degrees into Fahrenheit degrees, multiply by 9 and divide by 5; but as the 0° of the centigrade scale corresponds with 32° Fahrenheit, it is necessary to add 32 to the number found. To convert degrees Fahrenheit into centigrade, the process is reversed; 32 is subtracted, and the remainder is multiplied by 5 and divided by 9.

§ 12. *Measurement of pressure.*—All gases alter their volume if the pressure to which they are exposed is altered. The atmosphere, which extends upwards to a distance sometimes computed as 200 miles, presses on each square inch of surface of the earth at the sea-level, with a weight of about 15 lbs.; or on each square centimetre, with a weight of 1·033 kilograms. This weight is represented by a column of mercury 30 inches (more accurately 29·922 inches), or 760 millimetres long; or by a column of water nearly 34 feet in length, or 10,328 millimetres.

§ **13.** The pressure of the atmosphere and its variations are registered by means of the barometer; the most convenient form of barometer for ordinary purposes, where extreme accuracy is not required, is what is known as the siphon barometer. It consists of a tube of the form shown in fig. 6 filled with pure dry mercury. The tube, about 850 millimetres long, is sealed at the top before it is bent, by heating the end and drawing off the glass; the end is then rounded by heating it and blowing in at the end *B*, a drying tube being interposed between the mouth and the tube. The tube is then softened 50 millimetres from the end over an ordinary bat's-wing gas burner at *C* and bent as shown in the figure. The edges of the open end *B* are then rounded. It is secured by means of wire to a strip of plate-glass mirror, *D*, which may be procured at any glazier's for a few pence. The mirror should be graduated in millimetres at *A* and *B*. This is best done by a mechanician, but if necessary it may be done by the student by coating the mirror at these parts with bees'-wax, and ruling the divisions from a good metre measure on the bees'-wax with a needle. The divisions are then etched with hydrofluoric acid, by painting the scratched part with a camel-hair pencil, dipped in the acid.

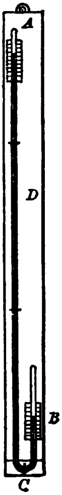

Fig. 6.

§ **14.** The tube is completely filled with mercury by pouring some into the limb *B*, and inclining it to make the mercury pass the bend. When nearly full, the thumb is placed on the open end *B*, and the bubble of air is made to pass up the tube till it reaches the top at *A*. It is then allowed to run up the tube, so as to sweep out all adhering air and finally escapes at *B*. By inclining the tube, the excess of mercury is poured out, until the level is nearly at the bottom of the bend at *C*, and the barometer is then secured to the mirror.

§ **15.** The best proof that the barometer does not contain air is to incline the tube somewhat suddenly, so as to cause the mercury completely to fill the tube at *A*. It should then be possible to bring it carefully to a vertical position without the mercury separating from the glass at *A*. The adhesion of the mercury to the glass causes it to remain in position, if no air is present; but if air is present it at once falls, when the tube is placed vertically. Should it be found to contain air, the process of sweeping out the air with a bubble must be repeated.

§ **16.** The object of the mirror at the back is to avoid parallax (see § 6). After tapping the tube, so as to render the meniscus of the mercury in both limbs equally convex, the top of the meniscus at *A* is made accurately to coincide with its reflection in the mirror behind, and the height is then read off, the tenths of a millimetre being estimated. This is repeated at *B*, and the number of millimetres read at *B* is subtracted from the number at *A*; the difference is the height of the column equal in weight to a column of air of equal section, extending to the top of the atmosphere; it represents the atmospheric pressure at the time of reading.

§ **17.** As mercury expands with heat, it follows that a column of warm mercury exerts less pressure than a column of an equal height at a lower temperature; and for purposes of comparison it is usual to reduce the actual height of the column to what it would be, were the temperature 0°.

If h be the observed height at temperature $t°$, h_0 the height reduced to 0°, and m the coefficient of expansion of mercury (=0·00018018), then the following equation is nearly correct: $h_0(1+mt)=h$, whence

$$h_0=h-hmt.$$

But temperature also affects the length of the divisions on the scale by which the height of the mercurial column is measured. For the purposes of this work, this correction may be neglected, as it affects only the second decimal point.

§ **18.** *Measurement of weight.*—Weight is measured by the *balance.* In weighing, the object to be weighed should be placed on the left-hand pan, or hung from the hook at the top of that pan, and a weight, judged equal to the object weighed, placed in the pan to the right. Should the weight prove too heavy, it is replaced in the box, and the next lighter one chosen. Should this be too light, the next heavier one is added, and so on. This process is repeated methodically until the pointer or needle rests at the middle of the scale.

In placing weights on, or removing them from the pan, the supports should always be raised, so that the beam may not be jarred. When the substance is as nearly balanced as possible with fixed weights, the rider is placed on the beam and adjusted. The support is then lowered, and a gentle breath of air is fanned with the right hand on the right pan of the balance; the case is immediately shut. The distance through which the pointer travels to the left is noticed, and the distance to the right. If these are equal, the weight of the substance has been ascertained. If not, the balance-case is opened, the rider re-adjusted, and a fresh swing given to the beam. This process is repeated until the pointer travels an equal distance to the left and right. The weights on the pan, and the position of the rider, are then noted, and their amount written down. The weights are then removed in order, the largest ones first, and while they are being replaced in the box their amount is again observed, and compared with the amount noted down. This rule should *always* be observed, or mistakes are certain to occur.

No substance should ever be weighed on the bare pan. This rule is stated, not merely for the sake of preserving the pans from injury, but because it saves the trouble of adjusting the balance so that the pointer shall always, when the balance is without weights on the pan, remain at the middle of the scale.

The substance should always be weighed on a watch-glass, tube, flask, crucible, or small beaker, according to convenience, and the weight of the vessel containing it ascertained and subtracted. If several portions of substance have to be weighed, it is convenient to place it in a small stoppered tube, and after weighing the tube and substance to pour out small portions successively, weighing between each removal. Thus, if three portions have to be weighed out, only four weighings are required. It is better not to attempt to weigh out an exact quantity, say 50 grams, as the time lost in weighing is generally greater than the time spent in calculating, if logarithms are used. Yet this rule has exceptions.

§ **19.** Weights, however well finished, are never perfectly exact. It must but seldom happen that a weight, professedly 1 lb., or 1 grm., has really exactly that weight. It also, moreover, seldom happens that the absolute weight of any object has to be determined. It is usually required to find the relation between the weights of two substances, and for this purpose it is sufficient if the weights employed to ascertain the weights of the substances are correct with regard to each other, i.e. if the 10-gram weight is exactly half of the 20-gram weight, and so on. The correctness of the weights is ascertained by placing on one of the pans one of the 1-gram weights, marked with a needle, near the number engraved on it, and counterpoising it on the other pan by shot, adjusting accurately with tin-foil, till the pointer of the balance makes equal excursions on each side of the zero-point. The 1-gram weight is then removed, and the other two, which should be marked 2 and 3 with a needle, successively placed on the pan, and their differences, if any, noted. A small slip of paper showing the excess or deficit of the weight should be pasted on the edge of the weight-box, or the balance-case. The 2-gram weight is then balanced against the two 1-gram weights, and the difference noted; the 5-gram weight against the 2+1+1+1 gram, and so on. The smaller weights are also balanced against each other.

§ 20. TABLE OF METRICAL MEASURES AND WEIGHTS.

LENGTH.

1 Metre = 10 Decimetres = 3 ft. 3·37 in.

1 Decimetre = 10 Centimetres = 3·937 in.

1 Centimetre = 10 Millimetres = 0·394 in.

AREA.

1 Sq. metre = 100 sq. decimetres = 1550 sq. in.

1 Sq. decimetre = 100 sq. centimetres = 15·5 sq. in.

1 Sq. centimetre = 100 sq. millimetres = 0·155 sq. in.

VOLUME.

1 litre = 1000 cubic centimetres = 1·761 pint = 61·027 cubic inches = 35·2154 fluid ounces.

1 cubic centimetre = 1000 cubic millimetres = 0·06103 cubic inches = 0·0352 fluid ounce = 15·4324 grain measures.

1 cubic millimetre = 0·01543 grain measure.

WEIGHT.

1 kilogram = 1000 grams = 2·2054 lbs. avoirdupois.

1 gram = 10 decigrams = 0·3527 oz. avoirdupois = 15·4324 grains.

1 decigram = 10 centigrams = 1·54324 grains.

1 centigram = 10 milligrams = 0·154324 grain.

The following numbers are easily remembered, and are approximately correct:

1 metre = 39 inches.
1 decimetre = 4 inches.
1 centimetre = $\frac{2}{5}$ inch.
1 millimetre = $\frac{1}{25}$ inch.

1 sq. metre = 10 sq. feet.
1 sq. decimetre = 15 sq. in.

1 sq. centimetre = $\frac{1}{6}$ sq. in.

1 litre = 1$\frac{3}{4}$ pints = 61 cub. in.
1 cub. centimetre = $\frac{3}{50}$ cub. in.

1 kilogram = 2$\frac{1}{5}$ lbs.
1 gram = $\frac{1}{31}$ oz. = 15 grains.
1 decigram = 1$\frac{1}{2}$ grains.

CHAPTER II.

RELATION OF THE VOLUMES OF GASES TO TEMPERATURE AND PRESSURE.

§ 21. It was remarked in § 1 that the volumes of all substances vary with the temperature, expanding when the temperature is raised, and contracting when temperature is lowered. The laws which govern the expansion of liquids and solids are as yet unknown; but the relation of the volumes of gases to temperature is a simple one.

The volumes of solids and liquids are scarcely affected by pressure. But as before, a change of pressure causes great alteration in the volume of all gases. The present chapter points out methods of proving experimentally changes of the volumes of gases when temperature and pressure are altered.

§ 22. *Expansion of gases by heat.—Law. All perfect gases, when heated, expand* $\frac{1}{273}$ *of their volume, measured at* 0° *C., for each rise of* 1° *C.* (*Charles and Gay-Lussac*).

Required to prove this law approximately for air, between the temperature of the room, and the boiling-point of water.

Apparatus.—A round-bottomed flask, of about 300 cub. cents. capacity. A tight-fitting red india-rubber cork, perforated with one hole. A glass tube, 5 centimetres long, inserted through the hole in the cork, so that its end is flush with the smaller end of the cork. A piece of thin black india-rubber tubing, 3 cms. long, slipped over the end of the tube. A spring clip on the india-rubber tube. A large iron pot.

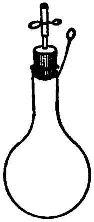

Fig. 7.

Experiment.—Cork the flask, so that the cork fits very tightly. Mark the position which the cork occupies, by drawing a line with a diamond or etching a line with hydrofluoric acid, so that the cork may always be pushed in to the same distance. Find the capacity of the flask and tube, by filling the flask quite full of water, and pushing in the cork to the mark, allowing the excess of water to escape through the india-rubber tube, while the clip is open. Measure the water which the flask contains, by transferring it to a graduated cylinder. Dry the flask *thoroughly* by waving it over the flame of a Bunsen's burner, and sucking out the air by means of a glass tube pushed into the flask. Replace the cork, which must also be dry, to the mark on the neck, and the clip on the india-rubber tube.

Boil some water in the iron pot, and push the flask into the water, so that it is completely covered by the boiling water, except the india-rubber tube; open the clip, to allow the expanded air to escape. Keep the flask in the boiling water for some minutes; then close the clip, lift out the flask, and dry it. Fill a large beaker, or a basin, with water. Place the flask, upside down, in the water, and open the clip. The air has cooled, and water will enter the flask. Lower the flask in the water, till the level of the water inside and outside is the same; (the object of this is to ensure that the air in the flask is in equilibrium with atmospheric pressure); close the clip. Read the temperature of the cold water. Dry the flask with a cloth, and after removing the cork, measure the volume of the water which has entered.

Calculation of results.

Capacity of flask	a
Water which has entered on cooling..............	b
Volume of air at lower temperature	$a-b$
Temperature of cold water	t

Temperature of boiling water .... 100°

Increase, ~~of~~ on volume measured at 0°, per degree $\frac{1}{x}$.

The relation to be found is as follows:—

Volume of cold air : volume of hot air

$$:: \left(1+\frac{1}{x}t\right) : \left(1+\frac{1}{x}.100\right).$$

Multiplying the two last terms by x,

$$a-b : a :: (x+t).:(x+100).$$

Whence $x = \dfrac{(100-t)a-100b}{b}$.

§ 23. *Alteration of the volume of a gas when pressure is altered.*

Law.—The volume of every perfect gas, provided temperature is constant, is inversely proportional to the pressure to which it is subjected (Boyle and Marriotte).

Required to prove this law approximately for air between the pressure of the atmosphere at the time of experiment, and a known reduced pressure.

Apparatus.—Similar to that described in § 22. Also a T-tube of narrow glass tubing of which the limbs of the cross piece are each about 5 cms. long, and the vertical limb about 40 cms. long. Another spring clip.

All gases, when in free communication with the atmosphere, are exposed to its pressure. This pressure is equal to that of a column of mercury of 720 to 780 millimetres in length, and is measured by the barometer. The method of experiment is to reduce the pressure below that of the atmosphere, and to ascertain how great a diminution in the volume of the air will be produced by raising the pressure to that of the atmosphere.

Experiment.—Connect one of the upper branches of the T-tube with the india-rubber tube from the flask; place a short piece of india-rubber tubing on the other branch, and let the long end of the T-tube dip into a small basin containing mercury. Open both clips. Exhaust the air in the flask by sucking air from the open india-rubber tube connected with the T-tube, closing the clip and resting occasionally for a few moments. When the mercury has risen to its highest attainable level, close both clips, and measure its height above that of the mercury in the small flask, with a metre measure, reading to millimetres. Disconnect the flask from the T-tube, taking care not to open the clip closing the flask. Then place the end of the india-rubber tube under water, and open the clip; and after having raised or lowered the flask, so that the level of the water is the same both outside and inside, close the clip, and measure the volume of the water which has entered the flask. Read the barometer.

Calculation of results.

Capacity of flask	a
Water which has entered	b
Volume of air under atmospheric pressure	$a-b$
Pressure of atmosphere	p
Height of mercury in T-tube	p'

The relation is found as follows :—

Vol. of air under reduced pressure.	Vol. of air under atmospheric pressure.	Pressure of atmosphere.	Reduced pressure.
a :	$a-b$ ::	p :	$p-p'$

whence $a(p-p')=p(a-b)$.

CHAPTER III.

AIR.

§ 24. *Weight of a litre of air.*

Exact determinations of the weight of a litre of air have shown it to be 1·293 *grams, at* 0°, *under* 760 *millimetres pressure.*

Apparatus.—A round-bottomed flask, fitted as described in § 22.

Experiment.—Pour about 30 cubic centimetres of water into the flask, and insert the cork to the mark. The india-rubber tube should be open, and the clip should be pushed down so as to close on the glass tube over which the india-rubber tube is slipped, in order that it may be ready when required. Boil the water in the flask, taking care not to use too large a flame, else the glass not in contact with the water will be heated, and will crack when water touches it. Let the steam blow out for about five minutes. Then close the india-rubber tube with the clip, and *immediately* remove the flame. Wipe the flask; allow it to cool, and weigh it, suspending it by means of a wire from the hook at the top of the balance pan. Note the temperature of the balance room, and the height of the barometer.

The air which was in the flask has been expelled by the steam, and the flask now contains only the vapour of water. Open the clip for some seconds. Weigh the flask again. The gain in weight represents the weight of the air which has entered. Lastly, measure the water which still remains in the flask.

Calculation of results.—It must be borne in mind that although the steam has expelled all, or nearly all the air from the flask, yet, even when the flask has cooled, the steam does not all condense, for water gives off vapour at all temperatures, although the lower the temperature, the less is evolved. When air is allowed to enter the flask, this water-vapour does not condense, but remains mixed with the air, and prevents so much air from entering as would enter if no water-vapour were present. It is therefore necessary to allow for its presence. The amount present depends on the temperature, and as the relation between temperature and evolution of vapour from water has been carefully examined, it would be possible to calculate its quantity and deduct the space which it occupies from the capacity of the flask. But it is found more convenient to represent its quantity by supposing it to alter the height of the barometer. If the temperature is high, then much vapour will be present, and a considerable deduction must be made from the height of the barometer; but if low the deduction is small. The accompanying curve shows the relation between the

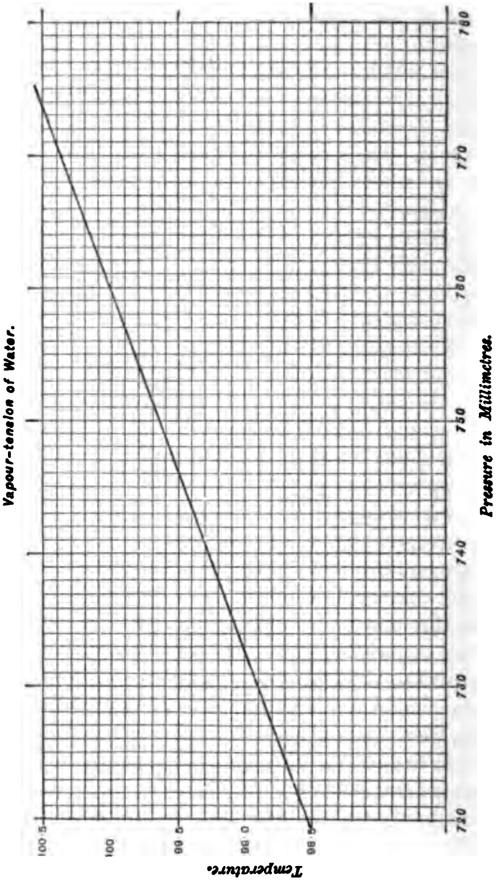
Vapour-tension of Water.
Pressure in Millimetres.
720
730
740
750
760
770
780
Temperature.
100·5
100
99·5
99·0
98·5

Fig. 8.

temperature and the number of millimetres which must be subtracted from the height of the barometer, in order to make this correction. This pressure is named the tension of water-vapour. It is one which will be employed, whenever it is necessary to measure a gas. The method of calculating is as follows:—

Total capacity of flask	a
Water remaining after experiment	b
Volume of air plus water-vapour	$a-b$
Temperature of atmosphere	t
Pressure of atmosphere	p
Weight of flask before air has entered	w
Weight of flask after air has entered	w'
Weight of air	$w'-w$
Tension of water-vapour	p'
Corrected volume of air	v
Weight of a litre of air at 0°	x

Then (1) $v=\dfrac{(a-b)\times 273\times(p-p')}{(273+t)\times 760}$,

(2) $x=\dfrac{1000\times(w-w')}{v}$.

Air contains two gases, oxygen and nitrogen, besides small amounts of carbon dioxide and ammonia, but the latter two constituents, owing to the small proportion in which they occur, may be neglected in these experiments. As air is a mixture, and not a compound, its specific gravity is equal to the product of the specific gravity of nitrogen into the percentage of nitrogen contained in air, plus the product of the specific gravity of oxygen into the percentage of oxygen contained in air, divided by 100.

The next exercise is to determine the composition of air by volume, and subsequently to ascertain the specific gravity of oxygen and nitrogen ; data are thus furnished for proving the truth of the above statement.

§ 25. *Composition of air by volume.*

Accurate analyses have shown that *air consists of* 20·9 *per cent. of oxygen by volume, and* 79·1 *per cent. of nitrogen.* The composition of air is not absolutely constant, but varies within narrow limits.

Apparatus.—A graduated tube. A tube, about 1 centimetre in external diameter is sealed at one end, and the knob of glass removed by softening it and blowing. The open end is heated in the flame, so as to round the sharp edges of glass. The tube is then warmed over a Bunsen's burner, and rubbed with bees'-wax till it is uniformly but thinly coated. From a burette, graduated in cubic centimetres, water is run in, 1 c.c. at a time, the level of the lower edge of the meniscus being indicated each time by making a faint scratch on the bees'-wax with a needle. Then place the tube between two pieces of wood, rather thicker than the diameter of the tube, and fasten them together with two india-rubber rings, and rule divisions on the waxed tube with a needle, making each division exactly coincide with the faint scratch. This done, write numbers on the tube to indicate the number of cubic centimetres, beginning at the closed end ; then paint the lines and the numbers with hydrofluoric acid solution; the acid should remain on the tube for about five minutes. The glass is thus etched. Warm the tube, after wiping it, over a Bunsen's flame, and clean off the wax. A piece of glass tubing, about 20 centimetres long and 3 millimetres in external diameter. A piece of thin copper wire, also about 20 cms. in length. A small basin. Some phosphorus.

Experiment.—The copper wire is pushed into the glass tube, and the phosphorus is placed in the basin, covered with water, and melted by a gentle heat. The glass tube is then dipped into the phosphorus, and the liquid element is sucked up the tube, great care being taken not to draw it up more than a few centimetres. Placing the tongue on the end of the glass tube, to prevent the phosphorus from running out, cold water is poured over the tube, so as to cause the phosphorus to solidify. When solid, it is removed, placed under water, and drawn out of the glass tube by means of the wire. Some water is next poured into the graduated tube, and placing the thumb on the end, it is inverted in water in a capacious trough, and sunk so that the level of the water inside and outside is equal. The tube is again closed with the thumb, removed from the water, and the volume of air which it contains is read off, the tenth of each division being estimated by eye. The tube is again placed in the trough, and the stick of phosphorus pushed up, so that it reaches to some distance above the level of the water in the tube. The tube is again closed with the thumb, removed from the trough, and placed in a beaker full of water. The temperature of the water in the trough, and the height of the barometer are noted. After two days, the tube is removed from the beaker, to the trough, as before, and the phosphorus withdrawn; and after the level of the water has again been adjusted, so that it is equal within the tube, and outside, the height at which it stands is again read off, temperature and pressure being noted as before. The residual gas now consists of nearly pure nitrogen, the oxygen having been absorbed by the phosphorus, which combines with it to form P_2O_3 and P_2O_5; these oxides of phosphorus dissolve in water forming phosphorous acid, H_3PO_3, and phosphoric acid, HPO_3, respectively.

As the air in the tube contains water-vapour, it is necessary to apply a correction so that its presence may not influence the results (see § 24).

Calculation of results.

Volume of air taken	a
Volume of nitrogen, after absorption of oxygen	b
Barometric pressure when the experiment is begun	p
Vapour tension at temperature t	p'
Temperature of water in trough when the experiment is begun	t
Barometric pressure when experiment is over	p_1
Vapour tension at temperature t'	p_1'
Temperature of water in trough when experiment is over	t'

To ascertain the original volume of the air, at 0° C. and 760 mms.

$$V = \frac{273 \times (p - p') \times a}{(273 + t) \times 760};$$

and of residual nitrogen,

$$V' = \frac{273 \times (p_1 - p_1') \times b}{(273 + t') \times 760}.$$

Then $V : V' :: 100 : x$.

§ 26. The composition of air by volume having thus been ascertained, it is next advisable to prepare the gases constituting air, viz. oxygen and nitrogen, and ascertain their specific gravity. During the preparation of oxygen, however, the reaction which occurs may be verified quantitatively.

§ 27. *Preparation of oxygen from potassium chlorate.*

When potassium chlorate is heated, oxygen is evolved, and potassium chloride and perchlorate are formed; on further heating, the latter body is also decomposed, with further evolution of oxygen, and potassium chloride remains. *From* 122·3 *grammes of potassium chlorate*, 47·9 *grammes of oxygen have been obtained* by very careful experiment, *measuring, at* 0° *and* 760 *mms.*, 33·52 *litres.* The reactions are:—

$2KClO_3 = KClO_4 + KCl + O_2$; and $KClO_4 = KCl + O_4$, or combining both

$$KClO_3 = KCl + 3O$$

$$\{39{\cdot}0 + 35{\cdot}4 + 47{\cdot}9\} = \{39{\cdot}0 + 35{\cdot}4\} + 47{\cdot}9.$$

Apparatus.—A short wide tube of hard glass, sealed at one end, and closed at the other with a perforated cork, from which a glass tube projects and is connected by means of india-rubber tubing with an aspirator. A graduated jar to collect the water expelled from the aspirator by the oxygen.

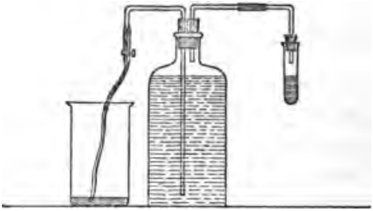

Fig. 9.

Experiment.—The hard glass tube, without being corked, is weighed; and about two grams of potassium chlorate are introduced, and the tube again weighed. It is then corked, and the apparatus arranged as shown in figure ~~1~~9. The tube is now heated to bright redness, and the water from the aspirator is received in the graduated jar or in a beaker. When gas ceases to be evolved, the tube is allowed to cool, the india-rubber tube conveying the water from the aspirator to the jar being allowed to dip under the water in the jar at the same level as the water in the aspirator, so that when the tube cools some water may be sucked back into the aspirator. The object of this is to ensure that the volume of the oxygen collected may be the same as that of the water received in the jar; if the precaution were neglected, the gas in the tube, being at a higher temperature than the air before commencing the experiment, would occupy a greater volume, and hence make the volume of oxygen evolved appear greater than it should be. The temperature of the air and the barometric pressure are noted.

Calculation of results.

Weight of $KClO_3$ and tube	a
Weight of tube alone	b
Weight of $KClO_3$ taken	$a-b$
Volume of water collected	v
Temperature of atmosphere	t
Barometric pressure	p
Tension of water vapour at temperature t	p'
Weight of KCl and tube after experiment	c

$$V = \frac{273 \times p - p' \times v}{(273 + t) \times 760}. \quad \text{And} \quad \frac{V \times 122{\cdot}3}{a-b} = x.$$

As before stated, x should equal 33·52 litres.

The weight of this oxygen will be found from the next experiment; but it may be found from the above data. For, $a-c$=weight of oxygen evolved, and the weight of a litre is given by the proportion,

$$V : 1000 :: a-c : x.$$

§ 28. *Weight of a litre of oxygen.*

The weight of a litre of oxygen is ascertained in exactly the same manner as the weight of a litre of air. The description in § 24 is almost completely applicable. The only point which may require explanation is the method of filling the flask with oxygen from the aspirator.

The india-rubber tube through which the water escapes from the aspirator is made to dip under water; and the flask, after air has been expelled by boiling the water, and it has been weighed, is connected with the other tube from the aspirator. The screw clip is then opened gradually, and the oxygen will enter the flask. The vessel containing the water, into which the india-rubber tube dips, is now raised so that the water it contains is at a higher level than the water in the aspirator; and the screw clip is closed. The flask is then disconnected, and the clip opened for a moment, so as to establish equilibrium of pressure between the oxygen and the atmosphere. The clip is then closed, and the flask weighed. The calculations are performed as in § 24.

Careful determinations have shown that *one litre of oxygen weighs* 1·429 *grams.*

§ 29. *Preparation of nitrogen.*—If oxygen gas is led through a strong solution of ammonia, and then over copper turnings heated to redness, the hydrogen of the ammonia combines with the oxygen, forming water, while the nitrogen of the ammonia passes on. The reaction is:—$2NH_3 + 3O = N_2 + 3H_2O$. By using air instead of oxygen, the nitrogen of the air is added to that of the ammonia.

Apparatus.—Aspirator full of very weak sulphuric acid. Hard-glass tube, filled with copper turnings, provided with a bored cork at each end. The one end is connected with the aspirator by means of india-rubber tubing, while the other end receives the exit tube of a flask, half-full of strong solution of ammonia. The arrangement is shown in figure 11. 10

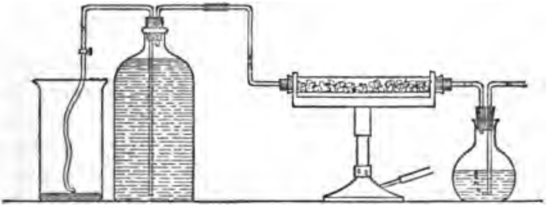

Fig. 10.

Experiment.—Heat the tube containing copper to redness. Then cause the dilute acid to flow out of the aspirator, drawing air through the ammonia solution. The gas which collects in the aspirator is nearly pure nitrogen. It is, however, mixed with a little ammonia gas, which will be dissolved by the dilute acid in the aspirator. About a litre should be collected.

§ **30.** *Weight of a litre of nitrogen.*—The weight of a litre of nitrogen is determined in exactly the same manner as described in §§ 24 and 28.

It has been found that *one litre of nitrogen weighs* 1·2553 *grams.*

§ **31.** It is now possible to find the relation of the weight of air to the weights of its constituents. The weight of a litre of air is 1·293 grams. Air consists of oxygen and nitrogen; the weight of a litre of the former is 1·429 grams, while a litre of the latter weighs 1·2553 grams. The percentage composition of air by volume is 20·9 p.c. of oxygen, and

79·1 p.c. of nitrogen. Hence its specific gravity should be

$$\frac{(20{\cdot}9 \times 1{\cdot}429) + (79{\cdot}1 \times 1{\cdot}2553)}{100} = 1{\cdot}2910,$$

a number closely approximating to that found by experiment. In performing the above calculation, the student should place the numbers found experimentally by himself in place of those given above, and try how closely the number found by the above calculation agrees with the weight of a litre of air, experimentally found.

It thus appears that *the weight of a litre of a mixture of two gases which have no action on each other is the mean of the weights of the two constituents expressed in centesimal proportion.*

CHAPTER IV.

HYDROGEN CHLORIDE, OR HYDROCHLORIC ACID GAS.

§ 32. *Weight of a litre of hydrogen chloride.*

It has been found that *one litre of hydrogen chloride under normal pressure and at normal temperature weighs* 1·6283 *grams.*

Apparatus.—A flask, fitted as described in § 22. A small flask, one-quarter full of common salt (sodium chloride, NaCl) provided with a perforated cork from which a tube issues bent at right angles. This tube is connected with a drying-bottle filled with strong sulphuric acid, with the exit tube of which is connected a tube about 50 cms. long.

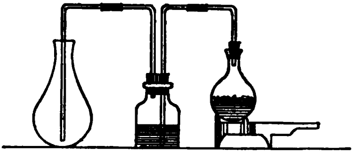

Fig. 11.

Experiment.—As hydrogen chloride is soluble in water, the flask, which should be perfectly dry, must be filled by displacing the air with the gas; for if the former method of ascertaining the weight of a gas were adopted, the hydrogen chloride on entering would dissolve in the water in the flask. As this gas is heavier than air, the flask must be filled by downward displacement. Arrange the apparatus as shown in fig. 11. Remove the cork and pour about 10 ccs. of strong sulphuric acid on to the salt, and replace the cork quickly. The following reaction takes place:— $NaCl + H_2SO_4 = HCl + NaHSO_4$. Hydrogen chloride will rapidly be evolved, and as soon as copious fumes issue from the mouth of the specific gravity flask draw out the tube gradually, and quickly insert the cork. Open the clip for a moment, to restore equilibrium with atmospheric pressure. Weigh the flask, and note the atmospheric temperature and pressure. The flask must then be opened under water, when the hydrogen chloride will rapidly dissolve in the water. Measure the amount of water which enters.

Calculations.

Total capacity of flask.......................... a
Temperature of atmosphere.................... t
Pressure of atmosphere .... p
Weight of flask with air....................... w
Weight of flask with hydrogen chloride ... w'
Weight of a litre of air .... 1·293 grams
Weight of a litre of hydrogen chloride ... x

(1) Find the weight of the air filling the flask.

It equals $\frac{a \times 273 \times p \times 1{\cdot}293}{(273+t) \times 760 \times 1000}$. Subtract this weight from w. The remainder is the weight of the vacuous flask. Subtract this weight from w'. The remainder is the weight of the hydrogen chloride, W.

(2) Find the volume of the hydrogen chloride at 0° and 760 mms.

It is $V=\frac{a\times 273\times p}{(273+t)\times 760}$. To find the weight of one litre,

$$x=\frac{W\times 1000}{V}.$$

§ 33. *Composition of hydrogen chloride by volume.*—Hydrogen chloride has been found to consist of *equal volumes of hydrogen and chlorine gases.* When this gas is treated with sodium, the chlorine combines with the sodium, and hydrogen is set free. Thus:—

$$HCl+Na=NaCl+H.$$

Instead of using metallic sodium, it is found more convenient to use sodium amalgam (an alloy of sodium and mercury); for when pure sodium is used, the surface soon becomes coated with salt, and the action is rendered a slow one.

Apparatus.—A graduated tube, as in § 25. The apparatus for generating hydrogen chloride, as in § 32. About 10 ccs. of liquid sodium amalgam, prepared by dropping a few fragments of sodium into hot mercury, contained in a porcelain basin.

Experiment.—Fill the graduated tube, which must be perfectly dry, with hydrogen chloride, just as the flask was filled in the last experiment. After withdrawing the long tube, close the open end with the thumb, and opening the tube for a moment, quickly pour in about 10 ccs. of sodium amalgam. Close the tube *at once* with the thumb, slightly moist, and shake well. Then invert the tube in a large beaker full of water, and remove the thumb. The amalgam will fall into the water, and water will rush up the tube, filling it nearly half full. After sinking the tube in water, so as to have the level equal inside and outside, in order to measure the hydrogen under atmospheric pressure, read the volume of the hydrogen gas. Then collect the mercury, and measure its volume.

Calculation.

Total capacity of tube.................. a
Volume of mercury .... b
Volume of hydrogen..................... c.

$$c=\frac{a-b}{2}.$$

§ 34. *Weight of a litre of chlorine.*—Exact experiments have shown *the weight of a litre of chlorine to be* 3·167 *grams.*

Apparatus.—The same as in § 32.

Experiment.—Place a mixture of equal weights of salt and manganese dioxide in the flask. Add sulphuric acid diluted with its own volume of water (by pouring the acid into the water), and cork the flask. Apply gentle heat. The chlorine evolved is led into the flask, and when full, which may be known by the yellow colour of the gas in the neck, the tube is slowly withdrawn, and the flask quickly corked. It is then weighed; and the atmospheric temperature and pressure are noted. As before, the flask must be dry.

Calculation.—Same as for hydrogen chloride (§ 32).

§ **35**. We now know that hydrogen chloride contains half its volume of hydrogen: that the weight of a litre of hydrogen chloride is 1·6283 grams: and that the weight of a litre of chlorine is 3·167 grams. It would be advisable to determine the weight of a litre of hydrogen, but this gas is so light as to render it impossible by means of such rough experiments to ascertain its weight with any accuracy. It is possible, however, to deduce it from the numbers already found. Thus, as hydrogen chloride contains half its volume of hydrogen,

$$\frac{1 \times 3{\cdot}167 + 1 \times x}{2} = 1{\cdot}6283 \text{ grams},$$

whence $x = 3{\cdot}2566 - 3{\cdot}167 = 0{\cdot}0896$ gram.

It is here presumed that the chlorine like the hydrogen also forms half the volume of hydrogen chloride. This is by no means proved by the experiments given; but if it form more than half the volume, for example if two volumes of chlorine unite with one volume of hydrogen, and contract to form two volumes of hydrogen chloride, the weight of a litre of hydrogen would be a negative quantity, which is absurd. No case is known in which expansion takes place when two gases combine, hence the chlorine cannot occupy less volume than the hydrogen. Experiment has shown moreover that when equal volumes of hydrogen and chlorine are mixed, and exposed to light or heat, they unite without a surplus of either chlorine or hydrogen.

§ 36. *Specific gravity.*—It is customary to compare the weights of gases with that of hydrogen or of air. For many reasons it is preferable to choose hydrogen as unity. The specific gravity, or weight compared with that of hydrogen, of air, nitrogen, oxygen, chlorine, and hydrogen chloride may now be found.

Hydrogen = 1·00.

(1) The specific gravity of air $= \frac{1·293}{0·0896} = 14·43$.

(2) " " " nitrogen $= \frac{1·2553}{0·0896} = 14·00$, nearly.

(3) " " " oxygen $= \frac{1·429}{0·0896} = 16·00$ "

(4) " " " chlorine $= \frac{3·167}{0·0896} = 35·34$.

(5) " " " hydrogen chloride $= \frac{1·6283}{0·0896} = 18·17$.

CHAPTER V.

WATER, OR HYDROGEN MONOXIDE, H_2O.

§ 37. *Weight of a litre of water-gas.*

As water boils at 100°, it is impossible to ascertain the weight of its gas by the process employed to determine the weight of hydrogen chloride and other gases which exist as such at ordinary temperatures. Hence in measuring the volume of the gas, it is necessary to heat it to temperatures above 100°. This can be done by immersing the flask in an oil-bath, heated above that temperature. But as it is difficult to maintain a uniform temperature by such means, the following process has been adopted, which obviates the difficulty.

The method is to cause the steam to displace its own volume of air; knowing the weight of water from which the steam has been formed, and the volume of the air, the requisite data are at hand.

Apparatus.—The flask used for the previous experiments. A well-fitting cork, perforated with two holes, one about 1 cm. wide, the other about 4 mms. A piece of glass tubing 10 cms. long, rounded at both ends, passing through the wide hole, and fitting accurately. Another tube fitting the narrow hole, bent at right angles as shown in figure 13. Some sand to place in the bottom of the flask. A small cork to close the wide tube. A piece of glass tubing about 1 cm. long, and 3 mms. in diameter, sealed at one end. The aspirator. A large iron pot with a lid in which a hole has been perforated large enough to allow the neck of the flask to pass through.

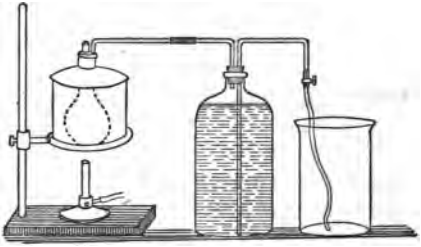

Fig. 12.

Experiment.—Weigh the short piece of tubing, first alone, then full of water. The weight of the water should not exceed 0·02 grm. Place the flask, with sand on the bottom in the pot, and insert the cork with the two tubes, the long one, its one end flush with the narrow end of the cork, passing through the hole in the lid of the pot, and connected with the entrance tube of the aspirator by means of a short piece of india-rubber tubing. Place the pot on a retort stand, and heat it with the full flame of a Bunsen burner. When some time has elapsed, the temperature of the pot will become nearly constant. Now drop in the small tube containing water through the wide tube of the flask, so that it falls on the sand, and quickly cork the wide tube. Water will quickly flow from the aspirator; it should be collected. As soon as the flow ceases, make the level of the water in the beaker coincide with that in the aspirator, and then uncork the wide tube and remove the flame. Measure the water, and read the temperature of the atmosphere and the barometric pressure.

Calculation.—The water collected is a measure of the air displaced from the flask by the water-gas evolved from the weighed amount of water.

Weight of glass tube and water	a
Weight of glass tube alone	b
Weight of water..	$a-b$
Volume of water collected	v
Temperature of atmosphere	t
Pressure of atmosphere	p
Tension of water vapour at t°	p'

Volume of water-gas supposed to exist at 0° and 760 mms. $\Big\} = \dfrac{273 \times (p-p') \times v}{(273+t) \times 760} = V.$

$$\text{Weight of 1 litre} = W = \frac{(a-b) \times 1000}{V}.$$

The weight of 1 *litre of water-gas at* 0° *and* 760 *mms. is* 0·8064 *grm.*

$$\text{Specific gravity of water-gas} = \frac{W}{0{\cdot}0896}.$$

The specific gravity is 9.

§ **38.** *Synthesis of water.—Water consists of* 8 *parts by weight of oxygen and* 1 *part by weight of hydrogen.* In this synthesis, hydrogen is passed over red-hot copper oxide; the copper oxide parts with its oxygen, which combines with the hydrogen, leaving metallic copper; the tube containing the copper oxide is weighed before and after the experiment; the difference in weight represents loss of oxygen; the water produced is collected by leading the steam through a tube filled with calcium chloride.

Apparatus.—A flask provided with a bored cork through which a tube is inserted, bent at right angles; this tube is connected by india-rubber tubing with the drying-bottle containing sulphuric acid; the drying-bottle is coupled with a piece of combustion tubing filled with copper oxide, and heated by a tube-burner; through a cork in the other end of the combustion tube is inserted a narrow tube, bent at right angles, passing through one of the corks of a drying-tube of a U-shape, containing calcium chloride. The aspirator filled with nitrogen.

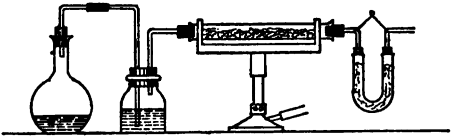

Fig. 18.

Experiment.—Place some granulated zinc in the flask, and cover it with about 100 ccs. of water. Fill the combustion tube with copper oxide, and draw air through it with the aspirator, so as to expel moisture; then let it cool, cork both ends, and weigh it. Fill the chloride of calcium tube, close both ends with short pieces of india-rubber tubing, stopped with pieces of rod, and weigh it. Connect the apparatus together. Before corking the flask, pour on the zinc about 20 ccs. of strong sulphuric acid. Now cork the flask, and when the hydrogen gas is being rapidly evolved, heat the tube containing the copper oxide. As soon as the red colour of the metallic copper has spread to within 5 or 6 centimetres of the end of the tube farthest from the flask, withdraw the cork and turn out the gas. While the tube is cooling, pass a current of nitrogen through it from the aspirator, to expel water-vapour from the tube. When cold, disconnect the apparatus, and cork both ends of the copper tube and of the chloride of calcium tube which has received the water, and weigh them.

Calculation.—The loss of weight of the copper oxide tube represents oxygen which has combined with the hydrogen. The gain in weight of the chloride of calcium tube is equivalent to the water produced. The difference between the gain of the latter and the loss of the former is due to hydrogen.

Weight of copper oxide tube before experiment ... a
„ „ „ after „ ... b
Oxygen lost .... $a - b$

Weight of chloride of calcium tube after experiment	c
Weight of chloride of calcium tube before experiment	d
Water produced	$c-d$

$$(c-d)-(a-b)=\text{Hydrogen in water.}$$

$$a-b=\text{Oxygen in water.}$$

$$\frac{(a-b)\times 100}{(c-d)}=\text{Oxygen per cent.}$$

$$\frac{(c-d)-(a-b)\times 100}{c-d}=\text{Hydrogen per cent.}$$

§ **39.** *Relations between the composition of water-gas by weight and volume.*—It has been now ascertained that water contains 88·88 per cent. of oxygen and 11·11 per cent. of hydrogen, and that the specific gravity of water-gas or steam is 9. As the specific gravities of oxygen and hydrogen gases are known (see § 36) it is possible to calculate the proportion by volume of the gases which form water by combining. Let us assume that we are dealing with 11·11 grams of hydrogen and 88·88 grams of oxygen. Now 11·11 grams of hydrogen must occupy 124 litres, for $\frac{11\cdot 11}{0\cdot 0896}=124$; and 88·88 grams of oxygen must occupy 62 litres, for $\frac{88\cdot 88}{1\cdot 429}=62$. We see therefore that the volume of hydrogen gas is twice as great as that of oxygen gas in the gaseous mixture required to produce water. But the specific gravity of such a mixture must necessarily be the mean of that of the two gases; a mixture of two volumes of hydrogen gas and one volume of oxygen gas should have the specific gravity

$$\frac{(1 \times 16) + (2 \times 1)}{3} = 6.$$

We should find that such a mixture possessed such a density. But such a mixture is not steam. We have found steam to possess the specific gravity 9, and it is evident that the numbers 9 and 6 have a very simple relation to each other. By the equation

$$\frac{(1 \times 16) + (2 \times 1)}{2} = 9,$$

we obtain the number 9 instead of 6. This means that when two volumes of hydrogen and one volume of oxygen *combine*, the volume of gas, which before combination was three times that of the oxygen contained in it, contracts, so that the volume of the compound water-gas occupies only twice the volume of oxygen contained in it. Hence we may state that *when two volumes of hydrogen combine with one volume of oxygen, two volumes of water-gas are formed.* This has been proved experimentally, first by mixing the gas in these proportions, and causing them to explode by heating them with an electric spark; they combine *totally*, neither being in excess; and second, by passing an electric current through water, when the gases are evolved in these proportions. From the negative electrode, that is, the one connected with the zinc plate of the battery, hydrogen is evolved;

and from the positive electrode, connected with the copper, or carbon plate of the battery, oxygen is evolved. By collecting these gases in graduated tubes it is easily seen that the hydrogen has a volume twice as great as the oxygen. These experiments are usually shown in the course of lectures on chemistry; and the method of performing them is to be found in all chemical text-books.

To sum up:—

Water consists of 2 parts by weight of hydrogen, and 16 parts by weight of oxygen. The specific gravity of its gas is 9 times that of hydrogen. It consists of two volumes of hydrogen and one volume of oxygen in combination, contracted to two volumes.

CHAPTER VI.

AMMONIA, OR HYDROGEN NITRIDE, NH_3.

§ **40.** *Weight of a litre of ammonia.*

Exact experiments have shown *the weight of a litre of ammonia to be* 0·7616 *gram.*

Apparatus.—The same as in § 32.

Experiment.—About 50 cubic centimetres of the strongest *liquor ammoniae* (solution of ammonia gas in water) is placed in the flask. The drying-bottle is filled with fragments of caustic lime as large as peas. As ammonia gas is lighter than air, the flask must be filled by upward displacement, that is, the delivery tube must be turned upwards, and the flask inverted over it as shown in figure 14. By gently warming the

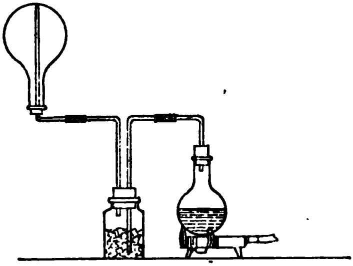

Fig. 14.

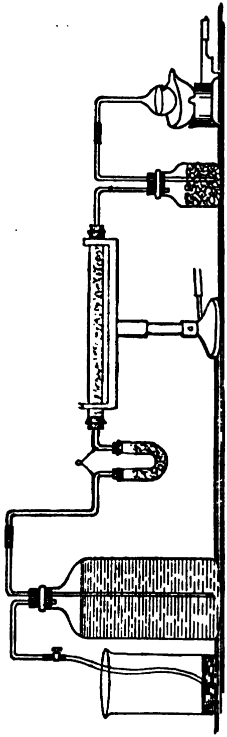

Fig. 15.

flask containing the ammonia, the gas is expelled from the solution, and escapes into the specific gravity flask. After some time, the latter is slowly raised, and as soon as the tube is removed, the flask is corked and weighed. The specific gravity flask must be thoroughly dry before it is filled with ammonia gas, else some gas would dissolve in the water, and the weight would seem greater than it really is.

Calculation.—Same as in § 32. Calculate also the specific gravity of ammonia compared with hydrogen as unity.

§ 41. *Composition of ammonia gas by weight.—Analysis of ammonia.*—AMMONIA *consists of* 3 *parts by weight of hydrogen and* 14 *parts by weight of nitrogen.* In this analysis, a known weight of the gas is led over red-hot copper oxide; the hydrogen combines with the oxygen of the copper oxide forming water, which is collected and weighed; from its weight the weight of the hydrogen which has served for its formation may be calculated, for we know the relative proportions of hydrogen and oxygen in water; while the nitrogen is collected in an aspirator, and its volume is measured by measuring that of the water which it displaces.

Apparatus.—A hard glass tube, 25 cms. long, filled with copper oxide, and closed at both ends by perforated corks, placed on a long-flame burner. Through one cork a piece of thin tubing passes, connected with the drying-bottle used in the last experiment filled with quick-lime which is in communication with a very small glass flask or bulb containing strong ammonia solution. One end of the combustion tube is connected with a tube filled with calcium chloride; and the other end of the calcium chloride tube is connected with the aspirator. See fig. 15.

Experiment.—The tube containing copper oxide is first heated, corked at both ends, then allowed to cool, and weighed. The drying-bottle and ammonia flask are weighed together. The chloride of calcium tube is also weighed, and the apparatus is arranged as shown in the figure. The tube containing copper oxide is then heated to redness, and the water in the aspirator is caused to flow, by opening the screw clip. The flask containing ammonia is then gently warmed by surrounding it with tepid water. The ammonia gas evolved is dried by the lime in the drying-bottle, and passes over the copper oxide, which is reduced at the end next the ammonia, showing the red colour of metallic copper. When this red colour is seen to within 5 or 6 cms. of the other end of the hot tube, the clip regulating the flow of water from the aspirator is closed and the apparatus disconnected. The gas is turned out, and the copper oxide tube corked while still hot, and when cool, weighed. The chloride of calcium tube and the ammonia flask with its drying-bottle are also weighed. The water which has escaped from the aspirator is measured. It is advisable to insert stoppers into short india-rubber tubes closing both ends of the calcium chloride tube and also the exit tube from the drying-bottle, so as to ensure protection from the moisture of the air in the first instance, and escape of ammonia in the second. Temperature and pressure are read.

Calculation.

Weight of ammonia flask and drying-bottle after experiment	a	grams
Weight of ammonia flask and drying-bottle before experiment	b	,,
Weight of copper oxide tube before experiment	c	,,
Weight of copper oxide tube after experiment	d	,,
Weight of chloride of calcium tube after experiment	e	,,
Weight of chloride of calcium tube before experiment	f	,,
Water collected from the aspirator	g	ccs.
Temperature of the atmosphere	t	
Pressure of atmosphere	p	
Vapour tension at temperature t (see § 24)	p'	

1. Hydrogen calculated from loss of weight of copper oxide tube. Loss of oxygen $= (c-d)$. As 8 grams of oxygen are *equivalent to* (i. e. combine to form water with) 1 gram of hydrogen, the weight of the oxygen used divided by $8 = \frac{(c-d)}{8}$ equals the hydrogen contained in the ammonia used.

Its amount per cent. is found thus :—

$$\frac{(c-d) \times 100}{8\,(a-b)} = H \text{ per cent.}$$

2. Hydrogen calculated from the water produced: Gain in weight of the calcium chloride tube $=(e-f)$. As 18 grams of water are obtained from 2 grams of hydrogen, or 9 from 1, the weight of the water divided by 9 gives the hydrogen from which it has been formed. Thus $\frac{e-f}{9}=H$. And $\frac{(e-f)\times 100}{9(a-b)}=H$ per cent. It is evident that (1) and (2) should give the same result.

3. Nitrogen. The volume of the nitrogen at 0° and 760 mms. is calculated thus:—$V=\frac{(p-p')\times 273\times g}{(273+t)\times 760}$. Its weight is obtained by multiplying by 0·0012553 (see § 36). And its percentage amount thus:—

$$\frac{V\times 0{\cdot}0012553\times 100}{(a-b)}=N \text{ per cent.}$$

Former exact experiments have shown ammonia to consist of 17·65 per cent. of hydrogen, and 82·85 per cent. of nitrogen.

§ **42.** It is possible from these data to calculate the *relative volumes of hydrogen and nitrogen which can be obtained from ammonia gas*, for the weight of a litre of each gas is known (see § 36). By dividing the percentage of hydrogen by 0·0896 (the weight of a litre of hydrogen) and the percentage of nitrogen by 1·2553 (the weight of a litre of nitrogen) numbers representing their relative volumes are obtained. Thus $\frac{17{\cdot}65}{0{\cdot}0896}=197$; and $\frac{82{\cdot}85}{1{\cdot}2553}=66$; numbers which bear to each other the proportions 3 : 1.

§ **43.** *Volume of nitrogen gas obtained from a known* *volume of ammonia:*—In this experiment, the hydrogen of the ammonia is oxidised by means of sodium hypobromite, NaBrO, according to the equation

$$3NaBrO + 2NH_3 = 3H_2O + N_2.$$

Apparatus.—The graduated tube. The apparatus used for preparing ammonia as in § 40. A small basin.

Experiment.—The graduated tube is first dried. Some strong solution of caustic soda is then placed in the basin, and about one cub. cm. of bromine added to it. This is best performed in a draught chamber, to carry off the vapours of the bromine. Sodium hypobromite and bromide are formed according to the equation $2NaHO + Br_2 = NaBr + NaBrO + H_2O$. The tube is then filled with ammonia gas by upward displacement, and when full, the long tube is slowly withdrawn, and the open end of the graduated tube at once closed with the thumb. It is then dipped under the surface of the sodium hypobromite in the basin, and the thumb removed. The hand should be immediately washed, for the caustic soda attacks the skin if allowed to remain in contact with it. Bubbles of nitrogen rise in the liquid in the tube, and the liquid also partially fills the tube. After action has ceased, the tube is removed from the hypobromite solution by closing the end with the thumb, and transferred to a tall cylinder full of water. The level of the water inside and outside of the tube is made to coincide, and the volume of the remaining gas is then read off. It will be found to amount to half the capacity of the graduated tube. Two volumes of ammonia gas, therefore, consist of one volume of nitrogen, and the remaining volume consists of hydrogen. But from § 42 we know that the relative proportions by volume of the two gases are 3 volumes of hydrogen to 1 of nitrogen. We therefore must conclude that 2 volumes of ammonia would yield when decomposed 3 volumes of hydrogen and 1 of nitrogen.

§ **44.** Let us compare this result with that deduced from the weight of a litre of ammonia gas. One litre has been found to weigh 0·7616 gram; and the density of ammonia gas compared with hydrogen is consequently $\frac{0{\cdot}7616}{0{\cdot}0896} = 8{\cdot}5$. A mixture of 1 volume of nitrogen and 3 volumes of hydrogen would have the density

$$\frac{(14 \times 1) + (1 \times 3)}{4} = 4{\cdot}25.$$

But the density found is $8{\cdot}5 = 4{\cdot}25 \times 2$. Hence ammonia differs in density from a mixture of nitrogen and hydrogen gases taken in the proportion of 1 to 3, but bears the simple relation to it of 2 to 1. But from § 43 it would appear that when three volumes of hydrogen and one volume of nitrogen are combined in ammonia a contraction to one half ensues. Therefore the density of ammonia should be

$$\frac{(14 \times 1) + (1 \times 3)}{2} = 8{\cdot}5.$$

This agrees with the experimental data.

CHAPTER VII.

ATOMS AND MOLECULES.

§ 45. IT was propounded by the Greek philosophers Leucippus and Democritus (460—400 B.C.) that matter is composed of atoms,—i.e. indivisible particles,—too small to be handled or seen, which are in continual motion. Lucretius in his poem *De Rerum Natura*—("Of the nature of things")—has preserved for us an account of this theory, as it was extended by Epicurus (340—270 B.C.). This conception of matter, however, was a mere opinion, not deduced from experiment or observation, and led to no definite theoretical or practical result.

But at the beginning of the present century, John Dalton, a Manchester schoolmaster, in order to account for the then recently discovered fact that compounds have invariably the same composition, revived the notion of atoms. Before his time, the processes of chemical analysis were very imperfect, and even Dalton himself generalised on imperfect data. But he grasped the facts known to him from the researches of others, and supplemented by himself, viz. that, for the most part, compounds had been found of invariable composition; and he suggested that this invariable composition is a necessary result of the theory of the atomic constitution of matter. Thus from the invariable composition of water, Dalton concluded that it is composed of one atom of hydrogen in combination with one atom of oxygen. He published an account of his theory in his *New Principles of Chemistry*, in the year 1808.

Dalton did not confine himself, however, to propounding this atomic theory, but endeavoured to ascertain the relative weights of the atoms. Atoms must be so minute as to be wholly invisible, even under the highest powers of the best microscope; and hence such minute portions of matter can never be weighed, however delicate the balance. But if it be granted that atoms combine with each other in simple proportions to form a compound, then it is possible to determine, not the absolute, but the relative weights of such atoms. For example, water, according to Dalton, contains one atom of hydrogen and one atom of oxygen. We have seen from § 38 that 8 parts of oxygen by weight unite with 1 part of hydrogen. Hence, according to Dalton, an atom of oxygen is eight times heavier than an atom of hydrogen. To the relative weights of the atoms he gave the name "atomic weights" and referred them to hydrogen as unity, for he found that of all the elements which he investigated, hydrogen was the one with the smallest atomic weight.

§ **46.** In the year 1809, a French chemist, Gay-Lussac, published a memoir on the combination of gases, in which he endeavoured to show that "they always combine in equal bulks, or one part of one, by bulk, with two or with three parts of the other." This has been proved to be the case (see §§ 33, 39, and 44). And in 1811, an Italian chemist named Avogadro propounded the hypothesis that *equal volumes of gases, at the same temperature and pressure, contain equal numbers of atoms.* But it is evident that this latter assertion cannot be reconciled with the numbers assigned by Dalton. For, in the case of water, we have seen from § 38 that one part by weight of hydrogen combines with eight parts by weight of oxygen; from § 39 that two volumes of hydrogen combine with one volume of oxygen; and from § 36 that oxygen is sixteen times heavier than hydrogen. If then Avogadro's hypothesis be accepted, two volumes of hydrogen must contain twice as many atoms as one volume of oxygen, and the relative weights of the atoms of hydrogen and oxygen cannot be in the proportion of 1 to 8, but of 1 to 16. Moreover the water-vapour produced has been found (§ 37) to weigh nine times as much as an equal amount of hydrogen, and from § 39 to occupy the same volume as the hydrogen from which it is formed. We are therefore led to the following contradictory conclusions:

(1) From Dalton's numbers:—that water consists of one atom of hydrogen weighing 1, and one atom of oxygen weighing 8.

(2) From Avogadro's hypothesis:—that one atom of oxygen is sixteen times heavier than one atom of hydrogen.

(3) From Gay-Lussac's law and Avogadro's hypothesis:—that one volume of water-vapour contains as many atoms as one volume of hydrogen, whereas we know that it must contain half as many again, for the water-vapour, containing both hydrogen and oxygen, occupies the same space as the hydrogen from which it is formed.

§ **47.** By modifying these hypotheses, however, such contradictory conclusions are avoided. It is only within the last twenty years that such modifications have been generally adopted; and even yet a few chemists, chiefly French, refuse to accept the changes now to be explained.

(1) Avogadro's hypothesis that equal volumes of gases contain equal numbers of atoms is not strictly true, and the explanation which follows was first suggested by him. In order to avoid the last contradictory statement of § 46, he assumed that there is an order of particles larger than atoms. To such a particle, composed of two or more atoms, the word *molecule*—little heap—has been applied. He supposed that the *molecule* of elementary gases such as hydrogen or oxygen consists of two *atoms*. When two volumes of hydrogen combine with one volume of oxygen to produce two volumes of water-vapour the real change which takes place is, that two *molecules* of hydrogen consisting of four *atoms*, act on one molecule of oxygen consisting

of two atoms, and that these three molecules, together containing six atoms, act on each other to produce two molecules of water-vapour, each molecule of which consists of three atoms. This conception is rendered clearer by a graphic representation.

$$\begin{array}{ccccccccc} \boxed{\mathrm{H} \mid \mathrm{H}} & + & \boxed{\mathrm{H} \mid \mathrm{H}} & + & \boxed{\mathrm{O} \mid \mathrm{O}} & = & \boxed{\mathrm{H_2O}} & + & \boxed{\mathrm{H_2O}} \\ 2 \text{ atoms} & & 2 \text{ atoms} & & 2 \text{ atoms} & & 3 \text{ atoms} & & 3 \text{ atoms} \\ 1 \text{ mol.} & & 1 \text{ mol.} & & 1 \text{ mol.} & & 1 \text{ mol.} & & 1 \text{ mol.} \end{array}$$

(2) If the above conception be true, then the fact stated by Dalton, that one atom of oxygen is eight times heavier than one atom of hydrogen, must be false. It is now generally accepted that an atom of oxygen is sixteen times heavier than an atom of hydrogen, and the difficulty is thus avoided. Graphically represented, the action shown is as follows :—

$$\begin{array}{cccccccccc} & \boxed{\mathrm{H} \mid \mathrm{H}} & + & \boxed{\mathrm{H} \mid \mathrm{H}} & + & \boxed{\mathrm{O} \mid \mathrm{O}} & = & \boxed{\mathrm{H_2O}} & + & \boxed{\mathrm{H_2O}} \\ \text{Weights:—} & 2 & & 2 & & 32 & & 18 & & 18 \end{array}$$

It is seen that all requirements are thus satisfied. The weight of the *molecule* of hydrogen is one-sixteenth of the weight of the *molecule* of oxygen; the atomic weight of oxygen is therefore 16; two volumes of water-vapour are produced from three volumes of the constituent gases; and a volume of water-vapour equal to that of the hydrogen which it contains consists of the same number of *molecules* as that of hydrogen.

§ 48. *Avogadro's hypothesis.*—It is possible to prove Avogadro's hypothesis from the laws of motion of matter, and the results of experiments described in

§§ 22 and 23. This will now be attempted in as simple a manner as possible[1].

It has been found (§ 22) that the volume of a gas is inversely proportional to the pressure to which it is exposed; and we have seen that in order to reconcile Dalton's numbers, Avogadro's hypothesis, and Gay-Lussac's law (see § 46), gases have been assumed to consist of *molecules*. It is believed that all bodies, whether solid, liquid, or gaseous, consist of such molecules, and that these molecules are in a state of continual agitation. The hotter the body, the more violent the motion of the molecules. If the body is solid, the excursions of the molecule never remove it far from its original position; the molecules of a liquid, however, are not similarly held in position, but are free to move in any direction, without returning to their original places, as is shown by diffusion; they cannot move more than a very small distance without encountering other molecules, and being deflected from the straight path which they would otherwise follow. The time spent by the molecules in collision, however, bears a larger proportion to the time spent in unimpeded motion than in gases which, on the other hand, consist of molecules, moving with great velocity, and as, during the greater part of their course, they do not hit one another, they move in straight lines, until a collision occurs between two molecules, when each has its direction changed, and starts on a new path.

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[1] For the following explanation the author is indebted to Clerk Maxwell's *Theory of Heat*, and to Naumann's *Thermochemie*.

If a gas is confined in any vessel, the walls of the vessel receive constant blows from molecules of gas. As the number of molecules in any visible space is very great, blow succeeds blow with such rapidity that the individual impacts cease to be recognisable as such; and it is the sum of all the blows received from the gas by the walls of the vessel, that constitutes *the pressure of the gas*. Provided that there are no currents of gas in the interior of a vessel, the pressure of the gas is equal in all directions, as has been experimentally found.

During the encounters between molecules, the velocity, as well as the path, of each molecule is constantly changed. We cannot therefore suppose any molecule to possess a definite velocity for more than a very minute duration of time. But if it were within our power to observe any one molecule for a long time, and to register its rate of motion after each encounter with another molecule or with the side of the vessel, it would be possible to determine its *average velocity*. Thus if a train were to travel at the rate of twelve miles an hour for the first quarter of an hour; at twenty miles an hour for the second; at thirty for the third; and at fifty miles an hour for the fourth quarter of an hour, its average velocity would be twenty-eight miles an hour; for $12+20+30+50=112$; and $112\div4=28$.

Similarly it is conceivable that the average velocity of each molecule in the vessel might be thus ascertained, and that the general average velocity of all the molecules might be found. It will afterwards be shown that the average velocity of the molecules of a gas remains constant so long as the temperature of the gas is unaltered.

§ 49. The *momentum* of any piece of matter in motion is the product of its mass into its velocity. The momentum of a given molecule of gas is therefore

$$MV,$$

where M represents its mass, and V its velocity. The *energy* (or power of doing work) which such a mass possesses, in virtue of its motion, is by the principles of dynamics equal to the quantity

$$\tfrac{1}{2}MV^2.$$

If two gases, the molecules of one of which have greater mass than the molecules of the other, be mixed, the two sets of molecules will exchange energy by their encounters, until the *average energy of motion*, or *average kinetic energy* of a single molecule of either gas is the same. Let the mass of a molecule of the one gas be M_1, and that of the other M_2, and let their respective average velocities be V_1 and V_2, then

$$\text{(1)} \qquad \tfrac{1}{2}M_1V_1^2 = \tfrac{1}{2}M_2V_2^2,$$

and therefore $\qquad M_1V_1^2 = M_2V_2^2.$

It has been stated that the molecules of a gas are moving in all possible directions. It is possible to resolve such irregular motion into components in three directions, and if the containing vessel be a cube, these directions are best conceived as parallel to the sides of the cube. Let the average velocity of a single molecule be V; and let its velocity in the vertical direction

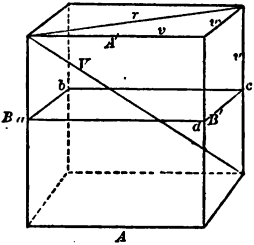

Fig. 16.

AA' or $A'A$, parallel to the plane of the paper, be u; and in the horizontal direction BB', or $B'B$, also parallel to the plane of the paper, v; and in a direction perpendicular to the plane of the paper, w; and let the number of molecules in a unit of volume be N. The number of molecules which will cross an imaginary plane *abcd* in a unit of time in the direction AA' will be Nu, as many molecules crossing the plane in the direction AA', as in the direction $A'A$, since the gas does not tend to accumulate on one side rather than on the other. The average momentum of each molecule in the direction AA' is Mu. Hence the momentum in this direction communicated to the region A in unit of time is, on each unit of area,

$$MNu^2.$$

As this bombardment of the side A' does not produce currents in the gas, it is manifested as pressure; and MNu^2 is therefore the measure of the pressure on the unit of area of the side A'. Similarly, the side A must suffer pressure, also equal to MNu^2 on every unit of its surface.

That the pressure involves the square of the velocity is easily realized by conceiving of a single molecule producing its pressure by blows alternating on opposite sides of the vessel. If its velocity is doubled, not only the momentum, but also the frequency of the blows is doubled, so that the quantity of momentum or pressure, communicated in the same time is not twice, but four times greater than before.

Now in the figure,

$$V^2 = u^2 + r^2, \text{ and } r^2 = v^2 + w^2,$$

(2) hence $V^2 = u^2 + v^2 + w^2$,

and V is the velocity of which u, v, and w, are independent components. But in every gas at rest, the pressure is equal in all directions, hence

(3) $u = v = w$; and $V^2 = 3u^2$.

Since $u^2 = \frac{1}{3}V^2$, the pressure of the gas on unit of surface is

(4) $p = \frac{1}{3}MNV^2$.

By reason of the numerous and varied encounters of the molecules with each other, individual molecules must exhibit the greatest diversity in their velocity and direction of motion. Hence at any given instant, single molecules must possess widely differing kinetic energies, $\frac{1}{2}MV_1^2$, $\frac{1}{2}MV_2^2$, $\frac{1}{2}MV_3^2$, etc., although the kinetic energy of the whole system remains constant. As regards pressure, however, the result is the same as if all the N molecules possessed the mean kinetic energy,

$$(5) \qquad \tfrac{1}{2}MV^2 = \frac{\frac{1}{2}MV_1^2 + \frac{1}{2}MV_2^2 + \frac{1}{2}MV_3^2 + \ldots\ldots}{N}$$

Most of the molecules will possess nearly this mean kinetic energy. Those which exceed the mean will be balanced by those which possess less energy, and comparatively few molecules will move with very much smaller or very much greater velocity.

From equation (4) it has been seen that the pressure on a unit of surface is equal to $\frac{1}{3}MNV^2$. Now, although the mass of a molecule and the total number of molecules in a unit volume are both unknown, yet the product of the two, MN, constitutes density, or weight of unit volume; for the mass of each molecule, multiplied by the number of molecules in a unit volume gives the mass of that volume, and density is the mass of a unit volume compared with some standard. Calling density ρ,

$$(6) \qquad p = \tfrac{1}{3}\rho V^2.$$

§ 50. Now the temperature of a gas is independent of its density. This has been experimentally proved by allowing a compressed gas to expand into a vacuum, whereby no alteration of temperature occurred. The density, that is the number of molecules in unit volume was thus altered, but there is no reason to suppose that in entering an empty space, the molecules undergo any change of velocity.

The temperatures of two portions of any one gas are equal when the one portion does not impart heat or energy to the other, that is, when the average kinetic energy, $\frac{1}{2}MV^2$, of the individual molecules of both portions of the gas is the same, whatever pressure they may be exposed to, or whatever their densities may be. If t_1 and t_2 represent the temperatures, and v_1 and v_2 the mean velocities of the two portions of gas, then if their temperatures are equal—if $t_1 = t_2$, the mean kinetic energies, $\frac{1}{2}MV_1^2$ and $\frac{1}{2}MV_2^2$, are also equal, since mean kinetic energy and temperature are identical; as $\frac{1}{2}M$ is common to both sides of the equation $\frac{1}{2}MV_1^2 = \frac{1}{2}MV_2^2$, it follows that $V_1^2 = V_2^2$. Hence it follows from equation (4), $p = \frac{1}{3}MNV^2$, that the pressure, p, is proportional to MN, that is (equation 6) to the density ρ, or to the number of molecules in unit volume, N. This has been experimentally proved in § 23, and is Boyle's law:—*The density of a gas is proportional to the pressure to which it is exposed;* or, *the volume of a gas is inversely proportional to the pressure to which it is exposed.* The correctness of the preceding reasoning is thus rendered probable, since the conclusion deduced coincides with experiment.

§ 51. The kinetic energy of the molecules $\frac{1}{2}MV^2$, mentioned in the preceding paragraph, is proportional to, and indeed is supposed to be identical with *temperature.* If the average velocity of the molecules be increased, we say the temperature is higher. We have seen from § 22, that if the temperature of a gas be raised it expands, and that its rate of expansion is $\frac{1}{273}$rd of its volume at 0° for each rise of 1° C. Now if a gas be cooled below 0°, it will contract $\frac{1}{273}$rd of its volume at 0° for each fall of 1°, until it liquefies, and then it will change its rate of alteration of volume entirely, for Gay-Lussac's law does not apply to liquids. Thus oxygen gas has been liquefied at – 113°, chlorine gas at – 34°; while bromine boils at 60°. Even before they reach the temperatures at which they liquefy, Gay-Lussac's law does not apply to them, and in so far they cease to be "perfect" gases.

Imagine a thermometer to contain gas, instead of liquid. Let this thermometer consist of a straight tube, graduated in cubic millimetres, and let its capacity be 500 cubic millimetres. Let this gas be confined under any constant pressure by a small thread of liquid such as water or mercury, which shall move in the tube without friction, and possess no weight, so that it does not exert pressure on the gas. When the gas is heated, then such a thread will act as an indicator and register the volume of the gas. Let this thermometer be so arranged, that when its temperature is 0° C. the gas will occupy 273 divisions of the scale,—in other words, will consist of 273 cubic millimetres. Now if this thermometer be heated to 1°, the indicator will stand at 274 divisions of the scale; if heated to 10°, at 283, if heated to 100°, at 373, and so on. The bottom of the tube is marked 0, and represents a point which the gas would reach were it cooled to − 273, if it did not change to liquid, and if it still followed Gay-Lussac's law. Such conditions are evidently impossible, and in practice such a temperature has never been reached. The temperature − 273° is, however, named the *absolute zero*, and *absolute temperature* is temperature measured from the absolute zero. Thus 0° C. represents 274° Abs.; 10° C., 280° Abs., and so on. The absolute zero is best conceived as at the bottom of a tube as described above. Thus we see that at 10° Abs. the volume of the gas is 10; at 30°, 30, and so on. In such a thermometer, the volume of the gas is proportional to the temperature measured on the absolute scale; always providing the pressure remains unaltered.

Now, a relation may be found between temperature and pressure as follows:—Suppose a gas under a given pressure p, and temperature t, to have a volume S. The temperature being increased to t', let the volume alter to S'. Keeping the temperature constant at its higher point, let pressure now be applied to decrease the volume S' to the original volume S. A relation is thus found; and experiment has shown that to decrease the volume of a gas from say 274 volumes to 273 volumes, the pressure must be increased in the proportion of 273 to 274. But a rise of temperature from 0° to 1° produces an expansion of volume from 273 to 274; hence *to maintain the volume of a gas constant when the temperature is raised requires an increase of pressure proportional to that rise of temperature measured on the absolute scale.*

From equation (4), $p=\frac{1}{3}MNV^2$, if the number of molecules in unit volume undergo no alteration,—if N is constant—the pressure is proportional to the mean kinetic energy of the single molecules, $\frac{1}{2}MV^2$.

As the pressure is proportional to $\frac{1}{2}MV^2$, so the absolute temperature is proportional to $\frac{1}{2}MV^2$; otherwise stated, ***the kinetic energies of two portions of the same gas, at different temperatures is proportional to these temperatures measured on the absolute scale:*** or

$$(7) \qquad \frac{\frac{1}{2}MV_1^2}{\frac{1}{2}MV}=\frac{273+t_1}{273+t_2}=\frac{T_1}{T_2},$$

where T stands for absolute temperature.

From equation (1) and the sentence preceding it, it has been seen that when two gases are mixed the different sets of molecules exchange energy until the average kinetic energy of a single molecule of either gas is the same. This is the expression of the fact that when two different gases at different temperatures exposed to the same pressure are mixed, the temperatures become the same and the pressure remains unaltered. From this it follows that unlike gases possess equal average kinetic energy when at the same temperature. Thus equation (8) becomes for two different gases,

$$(8) \qquad \frac{\frac{1}{2}M_1V_1^2}{\frac{1}{2}M_2V_2^2}=\frac{273+t'}{273+t_2}=\frac{T_1}{T_2}.$$

This is Gay-Lussac's law, proved experimentally in § 22.

§ 52. We have now seen that if M_1 and M_2 are the masses of individual molecules of two gases, and if V_1 and V_2 are the average velocities, their temperatures are equal when $M_1V_1^2=M_2V_2^2$, and the pressures of these two gases are represented by

$$P_1=\tfrac{1}{3}M_1N_1V_1^2, \text{ and } P_2=\tfrac{1}{3}M_2N_2V_2^2.$$

If these two gases exert the same pressure, then

$$M_1N_1V_1^2=M_2N_2V_2^2.$$

Their temperatures are represented by $M_1V_1^2$ and $M_2V_2^2$; if these are also equal, then $N_1=N_2$; that is, *the number of molecules in equal volumes of the gases at the same temperature and pressure is equal.* This is Avogadro's law, stated in § 46. The densities of the gases as shown in § 50 are equal to the mass of each molecule, multiplied by the number of molecules in unit volume :—

$$\rho_1=M_1N_1, \text{ and } \rho_2=M_2N_2.$$

As $N_1=N_2$, then $\rho_1 : \rho_2 :: M_1 : M_2$, or *the densities of two gases are proportional to the masses of their molecules, provided temperature and pressure be equal.* This is a necessary deduction from Avogadro's and Gay-Lussac's laws.

An extremely clear summary of this reasoning has been given by Professor Clifford; it is so lucid that it shall be quoted word for word :—

"If I have two [equal] vessels containing gas at the same pressure and the same temperature—suppose that hydrogen is in one, and oxygen in the other—then I know that the temperature of the hydrogen is the same as the temperature of the oxygen, and that the pressure of the hydrogen is the same as the pressure of the oxygen. I also know—because the temperatures are equal—that the average energy of a particle [molecule] of hydrogen is the same as that of a particle [molecule] of the oxygen.

"Now the [total] pressure [on the sides of each vessel] is made up by multiplying the energy by the number of particles [molecules] in both gases; and as the pressure in both cases is the same, therefore the number of molecules is the same."

§ 53. We see therefore that the molecular weights of gases can easily be compared by comparing the relative weights of equal volumes; but as the molecule of an elementary gas is, as a rule, composed of two atoms, the above comparison gives us generally the atomic, as well as the molecular weight. Hence, because oxygen is sixteen times heavier than hydrogen, and because a molecule, in each case, contains two atoms, the atomic weight of oxygen is sixteen times that of hydrogen. (A proof that a molecule generally consists of two atoms will be furnished later.)

Similarly, the atomic weight of nitrogen is 14, and of chlorine 35·4. And in the case of compound gases, the molecular weight is twice the specific gravity; for we have found experimentally in §§ 35, 37, and 42, that when more than two elements constitute a compound, contraction to "two volumes" always occurs. Thus hydrogen chloride consists of one volume of chlorine united with one volume of hydrogen, and the compound hydrogen chloride occupies two volumes; thus :—

$$\boxed{\mathrm{H}}\boxed{\mathrm{H}} \quad \boxed{\mathrm{Cl}}\boxed{\mathrm{Cl}} = \boxed{\mathrm{HCl}} + \boxed{\mathrm{HCl}}$$

And when two volumes of hydrogen unite with one volume of oxygen to form water, two volumes of water gas are produced.

$$\boxed{\mathrm{H}}\boxed{\mathrm{H}} + \boxed{\mathrm{H}}\boxed{\mathrm{H}} + \boxed{\mathrm{O}}\boxed{\mathrm{O}} = \boxed{\mathrm{H_2O}} + \boxed{\mathrm{H_2O}}$$

Similarly, two volumes of ammonia are formed from three volumes of hydrogen and one volume of nitrogen.

$$\boxed{\mathrm{H}}\boxed{\mathrm{H}} + \boxed{\mathrm{H}}\boxed{\mathrm{H}} + \boxed{\mathrm{H}}\boxed{\mathrm{H}} + \boxed{\mathrm{N}}\boxed{\mathrm{N}} = \boxed{\mathrm{NH_3}} + \boxed{\mathrm{NH_3}}$$

Hence a molecule of hydrogen chloride consists of an atom of chlorine in combination with an atom of hydrogen; a molecule of water-vapour of an atom of oxygen and two atoms of hydrogen; and a molecule of ammonia of an atom of nitrogen and three atoms of hydrogen. We are ignorant of the manner in which these atoms are combined; among other suggestions it has been supposed that they revolve round each other as planets revolve round a central sun; but of this there is no proof. All that is known is that the atoms in the molecule are in motion; and that by raising the temperature of the gas, that motion is increased. As regards the shape of the atoms and molecules, also, our knowledge is very deficient; the most probable supposition, on the authority of Sir Wm. Thomson, and one which agrees with the properties ascribed to atoms, is that they consist of matter in the shape of a ring, in constant vortex motion; this conception will be best realised from the following figure:—

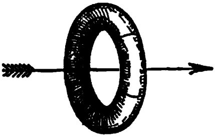

Fig.17.

However interesting such speculations may be, they are of little moment to the chemist, who has to deal with changes and with quantities rather than with forms.

CHAPTER VIII.

QUANTIVALENCE, OR VALENCY.

§ **54.** *Equivalents.*—From what has been stated in last chapter, it is to be noticed that one atom of the element chlorine combines with one atom of hydrogen; one atom of oxygen with two atoms of hydrogen; while ammonia consists of one atom of nitrogen in combination with three atoms of hydrogen. The word *equivalent* has been applied to denote the proportion of any element by weight which combines with or replaces one part by weight of hydrogen. Thus as 1 part of hydrogen by weight combines with 35·4 parts of chlorine, 35·4 is the *equivalent* of chlorine. Similarly 8 is the equivalent of oxygen, since 8 parts of oxygen combine with 1 part of hydrogen, for 8 : 1 :: 16 : 2. Also, 4·66′ is the equivalent of nitrogen, for

4·66′ : 1 :: 14 : 3.

§ **55.** *Quantivalence.*—The equivalent of an element always bears some numerical relation to its atomic weight. As a rule, this relation is a simple one. With hydrogen and chlorine, equivalent and atomic weight are equal; the atomic weight of oxygen is twice its equivalent; while that of nitrogen is three times its equivalent. It is found convenient to classify the elements according to the relation of equivalent to atomic weight. Elements such as hydrogen and chlorine, in which equivalent and atomic weight are equal, are named *Monads* (from *monos*, one). Those of which the atomic weight is twice the equivalent are named *Dyads* (*duo*, two), and those of which the atomic weight is three times the equivalent are named *Triads* (*tris*, three). Oxygen is an instance of a dyad, and nitrogen, in ammonia, of a triad. The word *Quantivalence* (literally, how much worth) or *Valency* is applied to denote generally the state of an element as regards its function as a monad, dyad, triad, etc. Thus we say the valency of hydrogen is 1, that of oxygen is 2, and that of nitrogen 3.

§ 56. As two elements often form more than one compound with each other, it is clear that in many cases an element must have more than one equivalent, and hence its valency or quantivalence is not always fixed, but variable. As a rule, monad elements have only one equivalent, but there are numerous exceptions. In the following paragraphs an experimental proof is given of the variability of the equivalency of the elements nitrogen and carbon, and it will be seen that nitrogen acts as monad in nitrogen monoxide or nitrous oxide, and as dyad in nitrogen dioxide or nitric oxide; while carbon is a dyad in carbonic oxide, and a tetrad in carbon dioxide or carbonic anhydride.

§ 57. *Preparation of nitrogen monoxide, and deter-*

mination of its specific gravity.—It has been found that *one litre of nitrogen monoxide weighs* 1·9712 *grams, at* 0° *and* 760 *mms. Its specific gravity is therefore* $\frac{1·9712}{0·0896} = 22$.

Apparatus.—The same as was described in § 32.

Experiment.—About 10 grams of ammonium nitrate are placed in the small flask; the tube issuing from the flask is connected with the drying-bottle filled with strong sulphuric acid; and the long tube connected with the drying-bottle passes to the bottom of the specific gravity flask, for nitrous oxide gas is heavier than air, and is therefore collected by downward displacement. A gentle heat is applied to the flask; the salt melts, and is decomposed according to the following equation into nitrous oxide and water :—

$$NH_4NO_3 = N_2O + 2H_2O.$$

It is essential that the heat be not raised too high, else further decomposition takes place. After some time, the tube is removed from the specific gravity flask; it is then corked and weighed. Its weight full of air and its capacity are then determined, and temperature and atmospheric pressure are noted.

Calculation.—Identical with that in § 32.

After finding the weight of one litre, the specific gravity is calculated as described in § 36 for other gases.

§ 58. *Analysis of nitrogen monoxide.*—Nitrogen monoxide consists of 28 parts by weight of nitrogen and 16 parts by weight of oxygen. In this analysis a quantity of the gas is led over red-hot copper; the copper is oxidised at the expense of the oxygen in the compound, while the nitrogen passes on, and is collected in an aspirator; its volume is that of the water collected from the aspirator. From the known weight of a litre of nitrogen, the weight of the volume collected can be ascertained.

Apparatus.—The flask and drying-bottle used for last experiment; a hard glass tube, 25 cms. long, resting on a long-flame burner. This tube is closed at both ends by perforated corks; one serves to connect with the drying-bottle, and the other to connect with the aspirator.

Experiment.—The nitrate of ammonium remaining in the flask from last experiment is gently and carefully heated; its products of decomposition, nitrous oxide and water, pass into the drying-bottle, where the latter is absorbed; the nitrous oxide gas passes over the combustion tube filled with copper turnings, (which has been previously weighed,) heated to redness, and the nitrogen is collected in the aspirator. Care must be taken that the portion of metallic copper nearest the aspirator does not lose its metallic lustre, else there is danger of some nitrous oxide escaping undecomposed. The stream of gas must not pass too quickly; the water should not run from the aspirator, but merely drop quickly. When some two or three hundred ccs. of nitrogen have been collected in the aspirator, the operation is stopped. The tube, now full of oxidised copper, is allowed to cool and weighed; and the water which has escaped from the aspirator is measured, temperature and pressure being noted.

Calculation.—1. *Oxygen.* The gain in weight of the tube containing metallic copper gives the amount of oxygen in the gas.. a.

2. *Nitrogen.* Volume of water collected ...... b
Temperature .... t
Pressure .... p
Vapour tension at temperature t (see § 24) .... p'.

$$V=\frac{a\times 273\times(p-p')}{273+t\times 760}.$$

The weight of the nitrogen is obtained by multiplying by 0·0012553 (see § 36). Let it equal c.

Then, $a : c :: 16 : 28.$

§ 59. *Specific gravity of nitrogen dioxide (nitric oxide).—One litre of nitric oxide has been found to weigh* 1·344 *grams; hence its specific gravity is* $\frac{1{\cdot}3440}{0{\cdot}0896}=15$.

Apparatus.—The same as that employed in determining the weight of a litre of nitrous oxide. The drying-bottle, however, should be filled with fresh sulphuric acid.

Experiment.—The flask in this experiment contains about 10 grams of copper turnings. After the various connections have been made, about 100 ccs. of a mixture of 1 part by volume of strong nitric acid and

2 parts of water are added, and heat is gently applied. Bubbles of gas are evolved, which immediately turn red on contact with the oxygen of the air. The reaction between the nitric acid and copper is as follows:—

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$$

It may be supposed that two reactions proceed simultaneously:

(1) $3Cu + 6HNO_3 = 3Cu(NO_3)_2 + 6H$. The hydrogen in the nascent state, i.e. while it is being "born" or liberated, when it probably consists of atoms uncombined to form molecules, reduces (deprives of oxygen) two molecules of nitric acid, thus:—

$$(2)\ 2HNO_3 + 6H = 4H_2O + 2NO.$$

The nitric oxide is collected by downward displacement, but as it has almost the same specific gravity as air, the current must be kept up for a considerable time. It is easy to know when the flask is full of nitric oxide, however, for when that gas comes in contact with air, red fumes are produced, in accordance with the equation:—

$$2NO + O_2 = 2NO_2.$$

When the contents of the flask are colourless, all air has been expelled, and the flask is filled with nitric oxide. It is advisable to perform this experiment in a draught-chamber, for the gas NO_2 has a most disagreeable smell, and is poisonous when breathed.

Calculation.—As in § 57.

§ **60**. *Analysis of nitric oxide.*—Nitric oxide consists of 14 parts by weight of nitrogen in combination with 16 parts of oxygen. It is analysed by passing it over red-hot copper, the gain in the weight of which indicates the proportion of oxygen it contains, while the nitrogen is measured.

Apparatus.—Similar to that employed for the analysis of nitrous oxide in § 58.

Experiment and Calculation.—Identical with that by which the composition of nitrous oxide is ascertained.

§ **61.** We have seen that nitrous oxide has the specific gravity 22; and it has also been seen that when two elements combine together, whatever their proportion by volume, gaseous compound always occupies two volumes. From § 52 we know that equal volumes of gases contain equal numbers of molecules; hence a molecule of nitrous oxide is 22 times as heavy as a molecule of hydrogen. But a molecule of hydrogen consists of two atoms; a molecule of nitrous oxide is thus 44 times heavier than an atom of hydrogen. This is otherwise expressed by saying that the molecular weight of nitrous oxide is 44. It has been proved to contain oxygen and nitrogen in the proportion of 16 to 28. This corresponds to a compound of one atom of oxygen, atomic weight 16, and two atoms of nitrogen, atomic weight $14 \times 2 = 28$; together equal to 44. And these two results confirm each other; hence we attribute to nitrous oxide the formula N_2O.

Similarly nitric oxide is 15 times as heavy as hydrogen, hence its molecular weight must be 30. It consists of 16 parts of oxygen, or one atom, combined with

14 parts of nitrogen or one atom. The sum of these weights agrees with that found, for 16 + 14 = 30. Thus by taking the specific gravity of a gas, its molecular weight is determined; were it not for this process, we could not know certainly the actual number of atoms in the molecule; nitrous oxide might have the formula N_4O_2, or N_6O_3, or any formula in which twice as many atoms of nitrogen are present as oxygen.

We have in nitrous oxide an instance of a compound in which nitrogen plays the part of a monad, for two atoms of nitrogen are in combination with one of oxygen; and in nitric oxide, nitrogen acts as a dyad, for one atom of nitrogen is combined with one of oxygen; and ammonia (see Chap. V.) contains triad nitrogen, for it consists of one atom of nitrogen combined with three atoms of hydrogen. A compound of the formula NO_2 is known, in which nitrogen functions as a tetrad; lastly in nitric anhydride, N_2O_5, and in ammonium chloride, NH_4Cl, nitrogen is a pentad. The equivalent of nitrogen is correspondingly variable; in N_2O, it is 14; in NO, 7; in N_2O_3 and in NH_3, 4·66 (14÷3); in NO_2 it is 3·5 (14÷4); and in N_2O_5 and in NH_4Cl, 2·8 (14÷5). It must never be forgotten that the atomic weight is a constant, however variable the equivalent may be. Few elements show such a varied valency as nitrogen; but there are also few which have not more than one equivalent.

§ 62. *Carbon monoxide* and *dioxide.*—Carbon forms two compounds with oxygen, in one of which, carbonic oxide, one atom of carbon is combined with one atom of oxygen; while in the other, carbonic anhydride, one atom combines with two atoms of oxygen. Both of these bodies have been quantitatively synthesised, by combustion of carbon with oxygen to form carbon dioxide, thus:—

$$C + O_2 = CO_2;$$

and also of carbon monoxide to dioxide:—

$$2CO + O_2 = 2CO_2.$$

In the former case, 12 parts by weight of carbon were found to require 32 parts of oxygen; and in the latter, 56 parts of carbon monoxide by weight required 32 parts of oxygen for complete combustion. These numbers will be taken for granted as correct, and the specific gravities of the gases will yield sufficient data for the conclusions to be drawn.

§ 63. *Specific gravity of carbon monoxide.*—Careful experiments have proved that *carbon monoxide is* 14 *times as heavy as hydrogen.* As carbon monoxide is so nearly the same weight as air, its collection by displacement is a very slow process. It is better to collect the gas in an aspirator and fill the flask from the store of gas.

Apparatus.—The specific gravity flask. A small flask like that used in the experiment described in § 58. The aspirator.

Experiment. (1) *Preparation of carbon monoxide.*—About 5 ccs. of formic acid are placed in the flask, and 50 ccs. of strong sulphuric acid are added. The aspirator is then completely filled with water. Gentle heat is now applied to the flask, and after bubbles begin to form, a considerable amount of gas is allowed to escape, so as to ensure expulsion of air from the flask. The exit tube is then connected with the aspirator by an india-rubber tube, and about a litre of gas is collected. The reaction by which the carbonic oxide is produced is

$$\underset{\text{Formic acid}}{H_2CO_2} - H_2O = \underset{\text{Carbon monoxide}}{CO.}$$

The water remains in combination with the sulphuric acid.

(2) *Determination of the specific gravity of carbon monoxide.*—About 25 ccs. of water are placed in the specific gravity flask, and boiled until air is expelled by steam. The clip is then closed, and the flask allowed to cool, and weighed. The exit tube is then connected with the exit tube for gas of the aspirator, and the other tube of the aspirator is allowed to dip into a beaker containing about 500 ccs. of water. The clip is next opened, when carbonic oxide will enter the specific gravity flask. The beaker is raised until the level of the water it contains is equal to that in the aspirator, and the clip is closed. The specific gravity flask is now disconnected and weighed.

Calculation.—The same as for air in § 24.

§ 64. *Specific gravity of carbon dioxide.*—Accurate experiments give 22 as the *specific gravity of carbonic anhydride.*

Apparatus.—A Wolff's bottle, or a flask closed with a doubly perforated cork; through one hole is inserted a funnel reaching to the bottom of the flask, through the other a tube bent at right-angles. The specific gravity flask. The drying-bottle.

Experiment.—Place some fragments of limestone, chalk, or marble in the Wolff's bottle or flask, and add about 100 ccs. of water. Insert the cork. Connect with the drying-bottle containing strong sulphuric acid. The exit tube from the drying-bottle should be joined to a long tube reaching to the bottom of the specific gravity flask, so that the gas is collected by downward displacement. The specific gravity flask should be dry, and its weight must be known.

Pour some dilute hydrochloric acid through the funnel. It reacts on the chalk, limestone, or marble, all of which are varieties of calcium carbonate, according to the equation

$$\underset{\substack{\text{Calcium}\\\text{carbonate}}}{CaCO_3} + 2HCl = \underset{\substack{\text{Calcium}\\\text{chloride}}}{CaCl_2} + H_2O + CO_2.$$

The carbonic anhydride is dried by the sulphuric acid, and is collected by downward displacement. When the specific gravity flask is full, it is corked and weighed.

Calculation.—See § 32.

§ 65. It has thus been proved that carbon monoxide has the specific gravity 14, hence its molecular weight is 28 (§ 61). It cannot contain less than one atom of oxygen; subtracting 16 from 28, the remainder is 12. The results of synthesis are thus confirmed. Similarly, the specific gravity of carbon dioxide, 22, leads to a molecular weight of 44. From synthesis it is known to contain twice as much oxygen as the monoxide; hence it must contain two atoms. Subtracting $2 \times 16 = 32$ from 44, the remainder is again 12. We cannot be absolutely certain that the atomic weight of carbon is 12, and not 6 or 3. But as no instance is known among the almost innumerable compounds of carbon, in which a smaller amount than one leading to the atomic weight 12 is contained, the probability is enormously in favour of this number as the correct atomic weight. We have here an instance in which it is possible to determine the atomic weight of an element which cannot be weighed in the state of gas, owing to the high temperature at which it volatilizes. If it forms gaseous compounds, or solid or liquid compounds which are convertible into gas at temperatures not exceeding 1000° C., it is possible to ascertain its atomic weight by the analysis of such compounds, and their specific gravity. This method is frequently resorted to.

§ **66.** Here again we have an instance of variable valency. In carbon monoxide, carbon plays the part of a dyad, and in carbon dioxide of a tetrad, for in the former case one atom of carbon is combined with one atom of oxygen, equivalent to two atoms of hydrogen; and in the latter with two atoms of oxygen, equivalent to four atoms of hydrogen. It is nevertheless remarkable that carbon monoxide forms the sole instance in which carbon can be conclusively shown to have a dyad character; in every other compound of which carbon is a constituent, it most probably functions as a tetrad (exceptions to this rule may possibly exist in fumaric acid, and in the isomeric citraconic acids, and perhaps in a few other cases; but of this there is no absolute proof). In carbon monoxide the equivalent of carbon is 6; and in carbon dioxide 3. In the former case the atomic weight is twice, and in the latter four times the equivalent.

CHAPTER IX.

EQUIVALENTS OF METALS.

§ 67. FROM last chapter it has been seen that the equivalent of an element is that weight which will enter into combination with one part by weight of hydrogen. It has also been shown that the equivalent is not a constant, but a variable quantity, and that the quantivalence or valency is expressed by the number of times which the equivalent is contained in the atomic weight. But it was also remarked that although most elements have variable valency, yet in the majority of their compounds they exist with a constant valency. This statement is more particularly applicable to metals, and may be illustrated by the following series :

	Cobalt.	Iron.	Chromium.	Aluminium.
Dyad.	Chloride $CoCl_2$	Chloride $FeCl_2$	Chloride $CrCl_2$	Unknown
	Oxide CoO	Oxide FeO	Oxide unknown	Unknown
	Sulphide CoS	Sulphide FeS	Sulphide unknown	Unknown
Triad.	Chloride ?	Chloride $FeCl_3$	Chloride $CrCl_3$	Chloride $AlCl_3$
	Oxide Co_2O_3	Oxide Fe_2O_3	Oxide Cr_2O_3	Oxide Al_2O_3
	Sulphide (Co_3S_4)	Sulphide Fe_2S_3	Sulphide Cr_2S_3	Sulphide Al_2S_3
Hexad.	Chloride unknown	Chloride unknown	Chloride (CrO_2Cl_2)	Unknown
	Oxide unknown	Oxide unknown	Oxide CrO_3	Unknown
	Sulphide unknown	Sulphide unknown	Sulphide (Cr_2S_7)	Unknown

It is to be observed that cobalt acts most readily as a dyad; its triad compounds are few in number and easily decomposed; it forms no hexad compounds whatever. Iron acts both as dyad and triad, although the compounds in which it functions as a dyad are better marked and perhaps more numerous than those in which it is a triad; while it shows a faint tendency to resemble chromium in its hexad character, a few very unstable salts, such as potassium ferrate, K_2FeO_4, having been prepared, derived from the unknown oxide FeO_3. Chromium forms very unstable chromous salts, in which it acts as a dyad; the chromic compounds, and the trioxide and its derivatives are stable. No dyad salts of aluminium are known; the compounds in which the metal acts as triad are the only ones.

It may therefore be stated that cobalt is usually a dyad; iron both dyad and triad; chromium seldom a dyad, usually a triad or hexad; and aluminium only a triad.

§ **68.** Some experiments will now follow, to show some methods of ascertaining the equivalents of metals. As metals do not as a rule combine with hydrogen, the equivalent must be ascertained indirectly. Either the chloride is analysed, and the relation of metal to chlorine found; knowing that chlorine is a monad, since it combines with an equal volume of hydrogen to produce hydrogen chloride, we arrive thus at the weight of metal required to replace hydrogen. Or this may be accomplished in a different manner. By dissolving the metal in hydrochloric acid the amount of hydrogen liberated as gas by a known weight of the metal may be estimated; the metal thus *displaces* its equivalent of hydrogen. Or the oxide of the metal may be deprived of oxygen by hydrogen at a red heat; the amount of water produced, and the loss of weight of the oxide both give the amount of oxygen which was in combination with the metal; and as one atom of oxygen is equivalent to two atoms of hydrogen, the equivalent of the metal can be calculated. Instances of these methods will now be given.

§ 69. *Equivalent of sodium.*—The sodium is alloyed with mercury, and then placed in dilute hydrochloric acid. Hydrogen is evolved, and collected. The reaction is $Na + HCl = NaCl + H$. *The equivalent of sodium is* 23.

Apparatus.—A flask closed with a well-fitting cork, perforated to admit a tube bent at right-angles, connected with the aspirator.

Experiment.—About 100 grams of mercury are accurately weighed in a counterpoised test-tube about 5 cm. in length. A piece of sodium about the size of a pea is cut into two or three small pieces and added to the mercury, the test-tube containing which should be gently warmed to cause the mercury and sodium to unite. The test-tube and mercury are again weighed, and the gain in weight represents the sodium amalgamated with the mercury.

The aspirator is now filled with water, and about 200 ccs. of water acidulated with hydrochloric acid are poured into the flask. The test-tube is then placed in the flask, which is corked, and the gas evolved collected in the aspirator. The water escaping from the aspirator is measured, temperature and pressure being read. As before, the exit tube from the aspirator is brought to the same level as the water in the aspirator before it is removed from the water collected.

Calculation.

Weight of test-tube, mercury and sodium ...	a
Weight of test-tube and mercury............	b
Volume of water collected	c
Temperature	t
Pressure	p
Vapour tension of water at temperature t ...	p'

(1) *Weight* of *hydrogen :*

$$W=\frac{273\times(p-p')\times c\times 0{\cdot}0896}{(273+t)\times 760\times 1000}.$$

(2) Equivalent of sodium :

$$Eq=\frac{(a-b)}{W}.$$

§ 70. *Equivalent of zinc.*—In this experiment, the zinc is dissolved in dilute hydrochloric acid, and the displaced hydrogen is collected. *The equivalent of zinc has been found to equal* 32·45.

Apparatus and experiment.—The apparatus is identical with that employed for the last experiment. The experiment is carried out in the same manner. About 2 grams of zinc are used, best distilled zinc, which is purer than the commercial metal. The hydrochloric acid should be stronger than that used in last experiment; about 1 part of fuming acid to 2 parts of water causes the reaction to take place sufficiently quickly. The equation is:

$$Zn + 2HCl = ZnCl_2 + H_2.$$

The calculation is performed as with sodium.

§ 71. *Equivalent of aluminium.—Found equal to* 9. A convenient quantity is 1 gram. The experiment and calculation are performed precisely as before.

§ 72. *Equivalent of silver.*—Silver does not dissolve in hydrochloric acid, for its chloride is insoluble in water and only very slightly soluble in hydrochloric acid. Its equivalent cannot therefore be determined by the method already given. It may be determined by heating the oxide, and collecting the oxygen evolved. The loss of weight of the oxide forms a check on the number obtained by collecting the oxygen. The reaction is $2Ag_2O = 2Ag_2 + O_2$. *The equivalent of silver is* 107·7.

Apparatus.—As in § 69; it is better however to use a smaller flask.

Experiment.—In order to ensure that the silver oxide is pure it is best to prepare it. For this purpose, baryta-water is added in excess to a solution of silver nitrate in a flask, by filtering the baryta-water into the flask, in order to prevent the absorption of carbonic acid by the baryta-water from the air. Silver oxide is precipitated according to the equation :—

$$2AgNO_3 + BaH_2O_2 = Ag_2O + H_2O + Ba(NO_3)_2.$$

The flask is immediately corked and shaken. The precipitated oxide settles quickly to the bottom. The cork is then removed and the liquid poured off as quickly and thoroughly as possible. Boiling water is then poured into the flask, which is again corked and shaken. The water is again quickly poured off, and the process is repeated five or six times. The excess of baryta and the barium nitrate, formed by the reaction, being soluble, are thus removed. The contents of the flask are then removed to a small basin, the last portions being washed out with distilled water; and the water is evaporated off over a water-bath; the temperature thus never exceeds 100°. From two to three grams of the oxide are weighed out, and placed in the small flask, which should be dried by warming it, and drawing air through it. The flask is then weighed. The cork is inserted, and the exit tube connected with the aspirator.

The flask containing the silver oxide is now heated, gently at first, then more strongly. Oxygen is evolved, and collects in the aspirator, metallic silver being left as a white powder.

Calculation.—Weight of silver oxide .... a
Weight of metallic silver ...... b
Volume of oxygen c
Temperature .... t
Pressure........................... p
Vapour-tension of water at temperature t .... p'

1. Equivalent $=\dfrac{b\times 8}{(a-b)}$.

The equivalent of oxygen is 8.

2. Weight of oxygen $=\dfrac{273\times(p-p')\times c\times 1{\cdot}4336}{(273+t)\times 760\times 1000}$.

Equivalent $=\dfrac{b\times 8}{W}$.

§ 73. *Equivalent of copper.*—The equivalent of copper is best determined by heating the oxide in a current of hydrogen; water is produced, and collected and weighed. This process is adopted since copper does not dissolve in acids with evolution of hydrogen, nor does its oxide part with oxygen easily when heated. *The equivalent of copper is* 31·6.

Apparatus.—A Wolff's bottle, or a flask with double-bored cork. Through one hole is inserted a glass funnel reaching nearly to the bottom of the bottle or flask; through the other hole is inserted the exit tube, bent at right-angles, and connected by means of india-rubber tubing with the drying-bottle filled with strong sulphuric acid. Instead of this arrangement, a Kipp generating apparatus may be used. From the drying-bottle a tube leads to a piece of combustion tube containing a weighed amount of copper oxide, and heated on a long-flame burner. The other end of the combustion tube is connected with a weighed tube containing calcium chloride.

Experiment.—Place about 30 grams of granulated zinc, or of sheet zinc cut into small pieces, in the Wolff bottle or flask, and add about 150 ccs. of water, and one drop of platinic chloride. Weigh the combustion tube; introduce about 3 grams of dry finely powdered copper oxide and weigh again. Weigh the tube containing fused calcium chloride. Connect the flask to the drying-bottle, and the latter to the combustion tube on the long-flame burner. Join the chloride of calcium tube to the combustion tube. Pour sulphuric or hydrochloric acid through the funnel in small quantity at a time so as to maintain a regular evolution of hydrogen. After the gas has escaped for some time, light the long-flame burner, and continue the current until the copper oxide has all been reduced to metallic copper: this will be known by its complete change to the red colour of copper. Notice that all moisture adhering to the cold end of the combustion tube is transferred to the chloride of calcium tube; if not, remove it by warming the combustion tube while the current of hydrogen is still passing. Put out the light; but continue to pass the hydrogen until the combustion tube is cold. Disconnect the apparatus; weigh the combustion tube and metallic copper, and the chloride of calcium tube.

Calculation.

Weight of combustion tube and copper oxide... *a*
Weight of combustion tube alone .... *b*
Weight of combustion tube and copper .... *c*
Weight of chloride of calcium tube after......... *d*
Weight of chloride of calcium tube before ...... *e*.

1. Oxygen from loss of weight of copper oxide :—

$$W=a-c.$$

2. Oxygen from gain in weight of chloride of calcium-tube: $W = \frac{(d-e) \times 8}{9}$. These two results should be identical.

3. Equivalent of copper $= \frac{(c-b) \times 8}{W}$.

§ 74. *Equivalents of tin.*—Tin has two equivalents; one may be ascertained by dissolving granulated tin, or *pure* tinfoil in a mixture of equal parts of hydrochloric acid and water, to which a drop of platinic chloride has been added to produce a galvanic couple between the metallic tin and the finely-divided platinum precipitated on the surface of the tin; the hydrogen gas evolved is collected in the aspirator. The whole process is carried out exactly as described for zinc in § 70. As hydrogen is evolved slowly from tin, it will be necessary to heat the flask, and to allow several hours for the evolution of the gas.

The second equivalent of tin is determined as follows:—About two grams of granulated tin are weighed out and placed in a small weighed evaporating basin. Five ccs. of strong nitric acid are then added cautiously, and the basin is placed on a water-bath in the fume closet. Red fumes of nitric peroxide are evolved, the nitric acid yielding oxygen to the tin. The excess of nitric acid is expelled by heat, and when the residue in the basin is apparently dry, the basin is removed from the water-bath and heated carefully over a Bunsen burner to dull redness. If the heat is cautiously applied, the basin will not break. When cold, it is weighed.

In the first case the equivalent is 58·85; *and in the second case* 29·42.

Calculation.—The calculation in the first instance exactly resembles that given for zinc in § 70; and in the second the process is as follows :—

Weight of tin oxide and basin......... a
Weight of tin and basin .... b
Weight of basin .... c.

Tin $= b - c$. Oxygen $= a - b$.

$$\text{Eq. of tin} = \frac{(b-c) \times 8}{(a-b)}.$$

§ 75. These are instances of the methods by which the equivalents of metals may be determined. They are not in every case the best or most accurate; but they exhibit the processes in their simplest forms, for they compare directly the weight of hydrogen which the metal replaces with that of the metal itself; or the weight of the metal with that of the oxygen with which it enters into combination. As the equivalent of oxygen in water is 8, it is easy to compare the metal with hydrogen through the intermediate element oxygen.

The next chapter will treat of the methods of determining the atomic weights of such elements, using as data the equivalents found, and the specific heats of the elements.

CHAPTER X.

SPECIFIC HEAT.

§ 76. In order to raise the temperature of a substance, heat must be communicated to it. The rise of temperature is coincident, as we have seen in the case of gases, with increased velocity of the molecules. As regards solids, the molecules have not the same freedom of motion as those of liquids and gases, but there can be no doubt that with the former also a rise of temperature implies greater molecular velocity, the path of the molecules being a very short one; in fact, it is supposed that the motion consists chiefly of rotation or vibration. Still the expansion of solids when raised to a higher temperature implies that the molecules are at a greater mean distance apart. Only a small fraction of the work done by heat is expended in overcoming the pressure to which the solid is exposed (atmospheric pressure); it is most probably spent in overcoming to some extent the cohesion of the molecules, which is *nil* with gases, considerable in liquids, and an important and distinguishing property of solids.

As yet, however, little is known as to the connection between the behaviour of solids when heated and their chemical nature. The most important relation which has been discovered is that between their specific heat and atomic weight.

§ 77. The specific heat of any substance, element or compound, is the amount of heat which must be communicated to it in order to raise its temperature through a given interval, compared with that required to raise the temperature of some standard body, through the same interval of temperature. The standard chosen is water. But the amount of heat which must be imparted to water to raise its temperature from let us say 4° to 5° C. is not the same, but a somewhat smaller amount than is required to heat an equal weight from 99° to 100°. This difference may be neglected in ordinary calculations, for it is a minute one. Accurately stated,

A unit of heat, or a calorie, is the heat which must be imparted to one gram of water to raise its temperature from 4° *to* 5° C.

It may be more conveniently, but not so accurately stated as the amount of heat required to raise the temperature of one gram of water through one degree.

It is also convenient to define specific heat in somewhat similar terms:—

The specific heat of a substance is the amount of heat expressed in calories which must be imparted to one gram, in order to raise its temperature through one degree.

As in the case of water, the specific heats of all substances vary with the temperature. At low temperatures, the specific heat is lower than that at higher temperatures.

§ 78. There are various methods of determining specific heat, many of which are much more accurate than the one which will here be described; but the results given by this process are sufficiently exact for our purpose.

It consists in mixing a known weight of the substance of which the specific heat is required, previously heated to a known temperature, with a known weight of water, also at a known temperature. The water will rise in temperature while the substance will cool. From the rise in temperature of the water, the number of units of heat or calories imparted to it can be easily calculated; it is equal to the number of calories lost by the substance. As the weight of the substance is known, it is easy to ascertain the amount of heat lost by one gram, and to compare it with the gain of heat of a gram of water. As this process is the same for all bodies which do not dissolve in water (when reactions take place which cause heat to be evolved or absorbed and influence the results) it will be described once for all.

§ 79. *Specific heats of the metals silver, zinc, aluminium, copper, and tin.*

Apparatus.—A thin beaker, surrounded with cotton-wool, holding about 200 ccs. of water. A test-tube about 2 cms. in diameter and 15 cms. long, round which a piece of wire has been twisted to serve as a holder. A large beaker. A thermometer. About 50 grams of the metal in turnings, filings, or borings.

Experiment.—The beaker, covered with cotton-wool, which is to serve as a calorimeter, or measurer of heat, is counterpoised, and 100 grams of water are then added. In weighing water or any liquid, it is convenient to add rather more than the desired quantity, and then withdraw the excess by dipping blotting-paper into it. Fifty grams of the metal are next weighed out, and placed in the test-tube. The large beaker is filled with water, and placed over a burner to boil. When boiling, the test-tube containing the metal is introduced into the water; the mouth of the test-tube being closed with a plug of cotton-wool. The temperature of the water in the calorimeter is then read as accurately as possible, tenths of degrees being estimated. After five or ten minutes, the metal in the test-tube may be presumed to be at 100°. The plug of cotton-wool is then removed from the mouth of the test-tube; the outside of the tube is rapidly wiped in order to remove adhering hot water; and the contents are transferred to the calorimeter as quickly as possible, the thermometer being removed for a moment. The water in the calorimeter is then stirred with the thermometer, the temperature being constantly observed; when it has reached its highest point, it is noted, tenths of degrees being again estimated.

Calculation.—The metal has been cooled from 100°

to the final temperature of the water, t_2, while the water has been heated from the initial temperature, t_1, to its final temperature, t_2. If its weight is 100 grams, it has gained $(t_2 - t_1)$ 100 units of heat. Fifty grams of the metal have lost $(100 - t_2)$ degrees of temperature. Hence the specific heat of the metal is found by the equation

$$(t_2 - t_1) \times 100 \times 1 = (100 - t_2) \times 50 \times x,$$

whence $$x = \frac{100\,(t_2 - t_1)}{50\,(100 - t_2)},$$

for the amount of heat lost by the metal in cooling through $(100 - t_2)$ degrees is equal to that gained by the water.

§ 80. The results obtained by this process are inaccurate, for the beaker used as a calorimeter absorbs some of the heat evolved by the hot metal, which would otherwise be communicated to, and raise the temperature of the water. And heat will be radiated from the beaker while the water is being heated by the metal, and consequently lost. It is to diminish this loss of heat that the beaker is wrapped round with cotton-wool; this substance encloses air, and prevents it circulating, and as air is one of the worst conductors of heat known, the particles of air in immediate contact with the beaker become hot, but do not readily communicate their heat to other particles; and if kept still, so that cold air-particles do not take the place of hot particles, but little heat is lost in this manner. It will be noticed, nevertheless, that in every case the specific heat found by this method is apparently lower than that found when precautions to ensure accuracy are taken.

§ 81. In the year 1819, two French chemists, Dulong and Petit, announced that they had discovered a simple relation between the atomic weights of 13 elements and their specific heats, and they formulated this relation as a law:—

The atoms of all elements in the solid state have the same capacity for heat.

Otherwise expressed, this states the fact that in order to raise an atom of all elements through the same number of degrees of temperature, the same amount of heat is required. Thus if 107·7 is the atomic weight of silver, and 63·2 the atomic weight of copper, exactly as much heat is necessary to raise the temperature of 107·7 grams of silver through one degree, as is required to raise the temperature of 63·2 grams of copper through one degree.

More recent investigations have shown this law to be only approximately correct; but it is sufficiently exact to afford great help in the determination of the atomic weights.

But this relation is somewhat involved, owing to the fact that the atomic weight of hydrogen is taken as unity, while specific heat is referred to the unit water. Referred to the standard of water, the specific heat of solid hydrogen is *in theory* 6·4, or some closely approximate number.

It is impossible, owing to the very low temperature at which hydrogen becomes a solid, to ascertain its specific heat experimentally, but it is inferred from other data. It is also customary to refer the specific heats of elements to the weight of 1 gram, instead of to the atomic weights of the elements. In order, therefore, to ascertain the atomic heat, or the heat required to raise atomic proportions of the elements through one degree, the number representing the specific heat must be multiplied by the atomic weight of the element. Thus the specific heat of tin has been found to equal 0·0548; that is, in order to raise one gram of tin through one degree, 0·0548 calorie must be imparted to it; or expressed differently, one gram of tin in cooling through 1°, will raise the temperature of 1 gram of water 0·0548°; but as the atomic weight of tin is 117·7, the atomic heat of tin is $0·0548 \times 117·7 = 6·45$—a number closely approximating to the theoretical atomic heat of hydrogen, $6·4 \times 1$. The atomic heat of tin is therefore equal to that of hydrogen.

§ 82. It may be asked—How is it known that 117·7 is the atomic weight of tin? On what is Dulong and Petit's law based? There are certain elements, of which tin is one, of which it is possible to determine the atomic weight by the method of vapour density. True, tin cannot itself be weighed as a gas, but several of its compounds can. The specific gravity in the state of gas of a compound of tin with chlorine, which has been found by analysis to contain 35·40 parts by weight of chlorine to 29·42 parts of tin, has been experimentally ascertained to be 132·85. Hence its molecular weight is 265·7 (see § 47). As 64·82 parts by weight of this chloride of tin contains 35·4 parts of chlorine, the atomic weight of tin can be ascertained by the proportion—

$$64{\cdot}82 : 35{\cdot}4 :: 265{\cdot}7 : x,$$

when x is found to equal 145·5. This is nearly equal to the weight of four atoms of chlorine, for

$$35{\cdot}4 \times 4 = 141{\cdot}6,$$

and it is therefore argued that this compound contains four atoms of chlorine. Subtracting from 265·7 this number, we obtain the number 124·1 as the atomic weight of tin, or a multiple of that weight. If the experiment had been more accurate, this number would have been 117·7, for 29·42 × 4 = 117·7. This result agrees sufficiently well with the result obtained from its specific heat.

From this and similar instances in which the atomic weight has been ascertained by such methods, it is argued that the law discovered by Dulong and Petit is approximately true in all cases.

§ **83.** It should here be mentioned that the specific heat of a compound is equal to the sum of the atomic heats of the atoms it contains. Thus the specific heat of lead iodide, containing as shown by analysis 206·5 parts by weight of lead to 253·1 parts of iodine, is 0·0427. Multiplying this number by 459·6, the molecular weight of lead iodide of which the formula is PbI_2, we obtain the number 20·1. This, it will be observed, is approximately 6·4 × 3. Hence, even in compounds, the atomic heat of elements is approximately a constant. The molecular weight cannot be thus determined; for were we to assume the molecular weight of lead iodide to be 919·2, corresponding to the formula Pb_2I_4, containing six atoms instead of three, we should get similar results: for

$$0{\cdot}0427 \times 919{\cdot}2 = 40{\cdot}2;$$

and

$$40{\cdot}2 \div 6 = 6{\cdot}7.$$

The molecular heat of a compound, then, divided by the number of atoms contained in the compound should again give a number nearly equal to the atomic heat of hydrogen, 6·4.

§ **84.** The atomic heats of some elements are abnormal. That of hydrogen, determined from the specific heat of its compounds is about 2·3; that of oxygen, 4; and of nitrogen, 5 to 5·5; and those of boron, carbon, and silicon, determined directly at low temperatures, are respectively about 3, 1·8, and 4·8; but it has been found that the higher the temperatures the more nearly they approach the number 6·4. Thus at 233°, the atomic heat of boron is 4·3; of carbon as diamond at 985°, 5·51; of carbon as graphite at 978°, 5·50, and of silicon at 232°, 5·68. It is generally to be noticed that elements of low atomic weight often show such abnormality: but the metals generally are normal as regards their atomic heat.

§ **85.** From the experiment described in § 79, it is possible to ascertain the true atomic weight of the metals silver, zinc, copper, aluminium, and tin. The numbers found should approximate to those which follow:—

Silver	0·0560
Zinc	0·0932
Copper	0·0930
Aluminium	0·0204
Tin	0·0560

These numbers have been found by careful experimenters using accurate processes.

Let us consider them one by one.

Silver.—As the atomic heats of elements are equal, their specific heats must be inversely proportional to their atomic weight; for

specific heat × atomic weight = specific heat of hydrogen.

Hence, specific heat of hydrogen ÷ specific heat = atomic weight.

Now, 0·0560 is the specific heat of silver. Dividing 6·4 by this number, we obtain the quotient 114. From § 72, the equivalent of silver has been found to equal 107·7. We know that the equivalent must be equal to the atomic weight, or must bear some simple fractional proportion to it. It is evident that 114 is much more nearly equal to 107·7 than it is to 107·7 × 2 or to 107·7 × 3. Hence *the equivalent of silver is identical with its atomic weight.* Silver is therefore a *Monad* in this oxide. Silver is found from other experiments to act almost invariably as a monad. Its chloride is $AgCl$; its oxide Ag_2O.

Zinc.—From § 70, the equivalent of zinc is 32·45. Now the specific heat of zinc is 0·0932. Hence

$$\text{Atomic weight of zinc} = \frac{6·4}{0·0932} = 68, \text{ approximately.}$$

But $68 = 32·45 \times 2$, approximately, therefore the atomic weight of zinc is equal to twice its equivalent. One atom of zinc thus replaces two atoms of hydrogen, and zinc is thus a *Dyad.* No compounds of zinc are known in which it possesses another valency. Chloride, $ZnCl_2$; Oxide, ZnO.

Copper.—The experiment in § 73 has shown copper to have the equivalent 31·6, and from § 79, its specific heat is 0·0930. Again $\frac{6·4}{0·0930} - 68$. This must be nearly the atomic weight of copper. This number is nearly $31·6 \times 2$, hence copper is also a *Dyad.* Compounds are known in which copper acts as a monad, e.g. Cu_2O, Cu_2Cl_2 or $CuCl$, etc.; but here its chloride is $CuCl_2$; its oxide, CuO.

Aluminium.—The equivalent of aluminium is 9 (§ 71). Its specific heat is 0·0214, hence its atomic weight approximates to $\frac{6·4}{0·0124} = 30$. This number more nearly equals 9×3 than 9×4. From this, and other considerations, the atomic weight of aluminium is regarded as 27, and as that number is three times the equivalent, aluminium is classed as a *Triad.* Chloride, $AlCl_3$; oxide, Al_2O_3. The valency of aluminium is invariable.

Tin.—The two equivalents of tin are 58·85 and 29·42. Its specific heat is 0·0560. Hence its atomic weight is $\frac{6·4}{0·056}=114$, nearly. But $114=58·85\times 2$, and $29·42\times 4$ nearly. Hence in the *stannous* compounds,—those in which least tin is contained proportionally to the other element with which it is in combination, tin is *Dyad;* while in the *stannic* compounds, it is a tetrad. The compounds $SnCl_2$, and SnO are instances of the former condition; $SnCl_4$ and SnO_2, of the latter.

BIBLIOTHECA BODLEIANA

CHAPTER XI.

METHOD OF DETERMINING ATOMIC WEIGHT BY "REPLACEMENT."

§ 86. *Replacement.*—If the equivalent of an element is known, but its atomic weight unknown or uncertain, the latter may sometimes be determined, or the results of other methods of determining atomic weight confirmed, by ascertaining in how many stages a monad element or group may be replaced by another element or group. Thus the element carbon, in its compound with hydrogen, methane, or marsh-gas, which contains the largest proportion of hydrogen of any compound of these two elements, is known to be a tetrad for the following reasons:—When methane is acted on with the monad element chlorine, the chlorine replaces hydrogen, giving successively three compounds containing both hydrogen and chlorine. As it is impossible that a smaller amount than one atom can exist in a compound, the conclusion is drawn that there are four atoms of hydrogen in methane which are replaced, one by one, by chlorine, thus:—

$$
\begin{aligned}
CH_4+Cl_2 &= CH_3Cl+HCl.\\
CH_3Cl+Cl_2 &= CH_2Cl_2+HCl.\\
CH_2Cl_2+Cl_2 &= CHCl_3+HCl.\\
CHCl_3+Cl_2 &= CCl_4+HCl.
\end{aligned}
$$

It is of course conceivable that in each of these reactions two atoms of chlorine replace two atoms of hydrogen, and that the formula of methane is C_2H_8, and not CH_4. But if that were so, its specific gravity should correspond with the formula C_2H_8, and be consequently 16; also the specific gravity of the compounds CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4 should be respectively 50·4, 84·8, 119·3, and 153·6, in which case the formulae would be $C_2H_6Cl_2$, $C_2H_4Cl_4$, $C_2H_2Cl_6$, and C_2Cl_8. But it has been found on experiment that the specific gravity of these substances is only half of the above numbers; these numbers therefore (§ 61) represent their molecular weights; hence the simpler formulae are chosen. The proportion by weight of carbon and hydrogen in methane is carbon 3, hydrogen 1. But from the preceding statement, it has been seen that the hydrogen is replaceable in four stages; hence this compound contains four atoms of hydrogen.

But this argument does not prove the formula to be CH_4. It still remains possible that methane contains two or more atoms of carbon. In such a case the atomic weight of carbon would be 6 or some smaller number, and not 12, and the formula of methane C_2H_4, C_3H_4, etc. So far as has been experimentally proved, there is no room for such a supposition. No attempt to replace the carbon in methane, or indeed in any compound of carbon, has been successful. A compound of the element silicon is known, to which, for reasons similar to those above stated, the formula SiH_4 has been attributed. If its formula were Si_2H_4, it might be reasonably expected that a compound containing both carbon and silicon of the formula $SiCH_4$ should exist. But no such compound is known.

These views are further supported by the fact mentioned in § 84, that the atomic heats of carbon and silicon at high temperatures are nearly normal.

§ **87**. This method has been successfully employed to determine the molecular weight of a group of elements, where no other method is applicable. Thus sulphuric acid is known to have the formula H_2SO_4, because the hydrogen which it contains is replaceable in two stages by metals such as potassium. The compounds are hydrogen potassium sulphate $HKSO_4$, and potassium sulphate K_2SO_4. The formula of phosphoric acid was formerly believed to be $P_2O_5 + 3H_2O$, or $H_6P_2O_8$. If that were the case, the hydrogen should be replaceable in six stages, with the formation of compounds such as the following :—

$$H_5KP_2O_8\,;\ H_4K_2P_2O_8\,;\ H_3K_3P_2O_8\,;\ H_2K_4P_2O_8\,;\ HK_5P_2O_8\,;\text{ and }K_6P_2O_8.$$

But of such compounds, only the second, fourth, and sixth are known; hence it is concluded that they have the formulae H_2KPO_4 dihydrogen potassium phosphate; HK_2PO_4 hydrogen dipotassium phosphate; and K_3PO_4 tripotassium phosphate, and that the formula of phosphoric acid is H_3PO_4.

As the group (PO_4) enters into combination with these monad elements, it is named a triad "radicle" or group. It may be combined with one dyad and one monad element, or with one triad element; in every case the three "affinities" or capacities for combination must be saturated. As instances, $CaHPO_4$, $AlPO_4$, etc. may ~~be adduced~~. Similarly the group $(HPO_4)^{II}$ is a dyad radicle; and $(H_2PO_4)^{I}$ a monad radicle. Bodies of this nature in which the hydrogen combined with the radicle is replaceable by metals are named acids. The capacity of replacement is termed the "basicity", and the acids are said to be "monobasic", "dibasic", or "tribasic" when they contain one, two, or three atoms of hydrogen replaceable by metals. Thus hydrochloric acid, HCl, and nitric acid, HNO_3, are monobasic; and hypophosphorous acid, H_3PO_2, although it contains three atoms of hydrogen is also a monobasic acid, for only one is replaceable by a metal. Sulphuric acid, H_2SO_4, and carbonic acid, H_2CO_3 are dibasic acids; and phosphoric acid, H_3PO_4, and hydroferricyanic acids, $H_3FeC_6N_6$ are tribasic acids.

§ 88. Compounds in which a metal replaces one or more atoms of the hydrogen of acids are named salts. If they still contain replaceable hydrogen, they are named *acid salts;* if all the hydrogen is replaced, they are termed *normal salts.* Thus $KHSO_4$ is an example of an acid salt; K_2SO_4 of a normal salt. The body KH_2PO_2 is a normal salt, for although it still contains hydrogen, yet that hydrogen is not replaceable by a metal. A dyad metal forms salts with a monobasic acid of the formula $M(A)_2$, where M is the metal and A the acid radicle. Thus calcium nitrate has the formula $Ca^{II}(NO_3)^{I}_2$. Similarly a triad metal forms salts with a monobasic acid radicle of which $Al^{III}(NO_3)^{I}_3$ is an instance; and with a dibasic radicle salts of which $Al^{III}_2(SO_4)^{II}_3$ is an example. Corresponding instances in which the metal is dyad and the acid radicle triad are to be found in $Ca^{II}_3(PO_4)^{III}_2$; $Mg^{II}_3(AsO_4)^{III}_2$, etc.

§ 89. The metals form a class of compounds in which it is convenient to regard them as replacing one of the atoms of hydrogen in water. Such compounds may also be viewed as double oxides of the metals and hydrogen. Thus the monad metal potassium forms the compound $K^{I}OH$, which may be regarded as an oxide of potassium and hydrogen, or as water, HOH, in which an atom of potassium has been substituted for an atom of hydrogen. The dyad metal iron forms a similar compound of the formula $Fe^{II}(OH)_2$, derived from two molecules of water, $H_2(OH)_2$; and the triad metal iron (for iron is both dyad and triad) gives the compound $Fe^{III}(OH)_3$, derived from $H_3(OH)_3$. A tetrad metal, such as tin, gives $Sn^{IV}(OH)_4$, derived from $H_4(OH)_4$. These compounds are so important and of such general occurrence that it has been found convenient to name the group $(OH)'$ "hydroxyl". This group has not been obtained free, for it would then resemble the atom of an element as contrasted with the molecule; but in combination with itself, $(OH)_2$, it is known as hydrogen peroxide.

Compounds of metals with hydroxyl are named *hydroxides* or *hydrates*. They are not acids, but react with acids forming salts, water being at the same time produced. The name "base" is commonly applied to such compounds: and they are termed mono-acid, di-acid, tri-acid, etc., when they contain one, two, or three groups of hydroxyl respectively. Thus KOH is a mono-acid base; $Ca(OH)_2$ a di-acid base; $Al(OH)_3$ a tri-acid base; etc.

§ 90. *Examples of reactions between acids and bases.*

(1) $KOH+HCl=KCl+H_2O$. Chloride.
(2*a*) $KOH+H_2SO_4=KHSO_4+H_2O$. Acid sulphate.
(2*b*) $2KOH+H_2SO_4=K_2SO_4+2H_2O$. Normal sulphate.
(3*a*) $KOH+H_3PO_4=KH_2PO_4+H_2O$. Monobasic or di-acid phosphate.
(3*b*) $2KOH+H_3PO_4=K_2HPO_4+2H_2O$. Dibasic or monacid phosphate.
(3*c*) $3KOH+H_3PO_4=K_3PO_4+3H_2O$. Tribasic phosphate.
(4) $Ca(OH)_2+2HNO_3=Ca(NO_3)_2+2H_2O$. Nitrate.
(5*a*) $Ca(OH)_2+H_2SO_4=CaSO_4+2H_2O$. Sulphate.
(5*b*) $Ca(OH)_2+2H_2SO_4=Ca(HSO_4)_2+2H_2O$. Acid sulphate.
(6*a*) $Ca(OH)_2+2H_3PO_4=Ca(H_2PO_4)_2+2H_2O$. Monobasic phosphate.
(6*b*) $Ca(OH)_2+H_3PO_4=CaHPO_4+2H_2O$. Dibasic phosphate.
(6*c*) $3Ca(OH)_2+2H_3PO_4=Ca_3(PO_4)_2+3H_2O$. Tribasic phosphate.
etc.

§ 91. It is also found convenient to regard acid bodies such as nitric, sulphuric, phosphoric acids, etc. as consisting of radicles or groups combined with hydroxyl. The number of such groups determines the *basicity* of the acid, just as the number of groups of hydroxyl combined with a metal depends on the quantivalence of the metal in the particular compound. Thus a monobasic acid contains one group of hydroxyl, in combination with an *acid radicle*; e.g.

nitric acid, $HNO_3 = (NO_2)^{I}OH$. The group (NO_2) is a monad group, and is regarded as analogous to an atom of a monad element. A dibasic acid contains a dyad radicle in union with two groups of hydroxyl; sulphuric acid, $H_2SO_4 = (SO_2)^{II}(OH)_2$. A triad radicle is supposed to exist in every tribasic acid; thus phosphoric acid, $H_3PO_4 = (PO)^{III}(OH)_3$, and so on. Acids which contain no oxygen of course contain no hydroxyl. But they may also be supposed to contain radicles in combination with hydrogen. For example, hydroferricyanic acid has the formula $H_3FeC_6N_6$, and it may be viewed as a compound of the triad radicle $(FeC_6N_6)^{III}$ with three atoms of hydrogen.

§ 92. Both metals and radicles combine with a radicle similar to hydroxyl, named hydrosulphuryl, $(SH)'$. Compounds of the metals with this group are named sulphydrates or hydrosulphides. As examples KSH, $Ba(SH)_2$, etc., may be cited. Certain radicles resembling those of the oxy-acids are also conveniently assumed to exist in the sulpho-acids; for example, $(CS)^{II}(SH)_2$, $(AsS)^{III}(SH)_3$, etc. Compounds such as calcium sulphocarbonate, $(CS)^{II}S_2Ca$, are named sulpho-salts; their analogy with oxy-salts is easily seen. Compare calcium carbonate, $(CO)^{II}O_2Ca$.

CHAPTER XII.

THE PERIODIC LAW.

§ 93. It was pointed out by Newlands in 1864 that if the elements be arranged in the order of their atomic weights in eight vertical rows, they fall into natural classes, each class containing elements resembling each other in the nature of their compounds, and in their usual valency. The relations of the atomic weights to other physical properties of the elements have been made a subject of research also by Mendelejeff, and by Lothar Meyer. This arrangement is shown on page 123.

§ 94. The elements in series 1 all form oxides of the formula R_2O where R represents any metal of the series. The gas hydrogen, probably a metal as shown by its compounds analogous to those of metals, as well as by its reputed appearance when solidified, differs considerably in the properties of its compounds from the remaining elements of its series. The metals lithium, sodium, potassium, rubidium and caesium all agree in the great tendency which they show to unite with oxygen, and in the solubility of their hydroxides, and generally speaking of their salts in water. The crystalline forms, outward appearance, and many of the

Series Group	1 R_2O	2 RO	3 R_2O_3	4 RH_4 RO_2	5 RH_3 R_2O_5	6 RH_2 RO_3	7 RH R_2O_7	8 R_2H RO_4
I.	H=1.0	—	—	—	—	—	—	—
II.	Li=7.0	Be=9.1	B=10.9	C=12.0	N=14.0	O=16.0	F=19.0	
III.	Na=23.0	Mg=24.0	Al=27.0	Si=28.2	P=31.0	S=32.0	Cl=35.4	
IV.	K=39.0	Ca=40.0	Sc=44.0	Ti=49.8	V=51.2	Cr=52.0	Mn=53.9	Fe=55 9 Ni=57.9 Co=58.9
V.	Cu=63.2	Zn=64.9	Ga=68.8	?=72	As=74.9	Se=78.8	Br=79.8	
VI.	Rb=85.2	Sr=87.4	Y=89.8	Zr=89.4	Nb=94.0	Mo=95.5	?=99 0	Ru=104.2 Rh=104.0 Pd=105.7
VII.	Ag=107.7	Cd=111.8	In=113.4	Sn=117.7	Sb=120.0	Te=128	I=126.6	
VIII.	Cs=132.6	Ba=136.7	La=139.0	Ce=141.6	Di=146.6	Tb=148.8	?=150	?=147
IX.	?=150	?=156	?=159	?=162	Er=165.9	?=167	?=169	
X.	?=170	?=172	Yb=172.8	?=180	Ta=182.1	W=183.6	?=190	Ir=192.6 Pt=194.4 Os=198.5
XI.	Au=196.2	Hg=199.7	Tl=203.7	Pb=206.5	Bi=210.0	?=214	?=219	
XII.	?=222	?=227	?=230	Th=233.4	?=237	U=238.5	?=244	

physical properties of their salts also point to close analogy between them. The metal copper, besides forming a monoxide, Cu_2O, with some corresponding salts, unites with oxygen to give a dioxide, Cu_2O_2, usually written CuO; this is also the case with the metals previously mentioned. The salts of cupric oxide, CuO, are more stable and better known than those of the cuprous oxide, Cu_2O; but salts of the dioxides of the "alkaline metals," Li, Na, K, Rb and Cs are unknown. Many of the salts of copper are insoluble in water; and in this they differ from those of the alkaline metals.

Silver agrees with the alkaline metals in the formulae of its salts; but the latter possess properties more analogous to those of copper. Thus silver chloride, bromide and iodide, $AgCl$, $AgBr$, and AgI present analogies in physical properties with $CuCl$, $CuBr$, and CuI; the sulphides of silver and of copper resemble each other; and the metals may be liberated from their compounds with comparative ease. Gold, Au, also forms an oxide of the formula Au_2O, but its higher oxide has not the formula Au_2O_2, but Au_2O_3. There is little analogy between the two metals gold and silver except in the physical properties of the metals themselves.

Passing to the next series, the first metal, beryllium, stands apart, resembling the others merely in the affinity which it has for oxygen and generally for the non-metallic elements. In this respect it may be compared with lithium, which presents a greater difference from sodium, potassium, rubidium, and caesium than these elements do from each other. The three metals, calcium, strontium, and barium are closely analogous. The physical properties of the metals themselves are similar; they all form insoluble or nearly insoluble sulphates; the crystalline form of their salts is in many cases identical and their hydroxides are all more or less soluble in water. The oxides unite directly with water, to produce the hydroxides, and it is impossible, or at least requires an extremely high temperature, to expel the elements of water from the hydroxides, reproducing the oxides.

Magnesium, zinc and cadmium form a similar group. All these metals resist oxidation by oxygen at the ordinary temperature; they differ from the metals calcium, strontium and barium in the solubility of their sulphates; the sulphates resemble each other in their crystalline form; the sulphides of zinc and cadmium are stable in presence of water; the hydroxides are not produced by direct union of the oxide with water, and water is easily evolved from the hydroxides by heat.

The remaining metal of this series, mercury, has no close resemblance to those previously mentioned, but has more analogy with silver and gold. It is difficult to combine with oxygen; it forms a hydroxide decomposed by a moderate heat; it forms a black sulphide, insoluble in acids; and the mercurous salts, of which an example is $HgCl$, or Hg_2Cl_2, resembles the corresponding silver salt.

It should be added that the metals calcium, strontium, and barium act as tetrads in forming compounds with oxygen of the formulae CaO_2, SrO_2 and BaO_2; these oxides, however, do not form corresponding salts; thus $Ca(SO_4)_2$, $CaCl_4$, etc. are unknown.

§ 95. The resemblance between boron, the first member, and the other members of the third series is a slight one. Indeed, boron more closely resembles silicon than any other element. Both are isolated as elements in the same manner; the elements themselves possess similar physical properties; and their compounds closely resemble each other. Neither boron nor silicon forms compounds with acid radicles, and both form oxides which combine with the oxides of metals forming salts, which also closely resemble each other in physical properties, while differing in character from almost all other salts. Yet in spite of these resemblances, the compounds of boron exhibit the element invariably as a triad, while silicon is no less unmistakeably a tetrad.

The metals aluminium, gallium, and indium form an analogous and parallel series to magnesium, zinc, and cadmium; it is also somewhat remarkable that aluminium and magnesium are often found associated, and gallium and zinc, and indium and cadmium also accompany each other. Scandium, yttrium, lanthanum, ytterbium, cerium, and didymium are also almost invariably associated; they are all rare metals, and are so similar in their behaviour that their separation is a matter of extreme difficulty.

Thallium, like mercury in the preceding series, has no striking resemblance to the other elements of its series. It partakes of the properties of the metals potassium and sodium, inasmuch as it forms *thallous* compounds in which it acts as a monad (e.g. $TlCl$, Tl_2SO_4, etc.), and these compounds bear a strong resemblance to the corresponding compounds of silver, potassium and sodium. The metal itself resembles lead; yet the *thallic* compounds ($TlCl_3$, $Tl_2 3SO_4$) possess a character of their own. Thallium shares with gold the property of acting both as a monad and as a triad.

Passing now to the fourth series, the first member, carbon, occupies a unique position. Although it exhibits certain analogies with silicon, and with the other elements of its series, yet the resemblance is caused more by its sharing their tetrad character than by any real likeness. There is no element which is known to form so many and so varied compounds. The compounds which it has the capacity of forming with hydrogen, oxygen, and nitrogen alone are apparently inexhaustible in number, while their nature is so varied that they afford all that complexity which appears to be necessary to the existence of life. From simple bodies such as carbon dioxide and marsh-gas, containing only one atom of carbon, to complex bodies such as chlorophyll, the green colouring matter of plants, and albumen, the basis of all animal life, which contain probably more than a hundred atoms of carbon, its wonderful power of producing compounds of the greatest diversity of function may be inferred. From this circumstance it is customary to treat of the compounds of carbon by themselves, and from the fact that they enter into the constitution of all organised beings, this branch has been named *Organic Chemistry.*

The elements silicon, titanium, and zirconium are analogous to each other. The chlorides are all volatile liquids; the oxides are all white insoluble powders; and these oxides when united with water form bodies partaking of the nature of acids, and forming salts which possess similar physical properties. The fluorides are also well characterised, and have the power of uniting with other fluorides forming double salts with well-marked properties. All these elements act only as tetrads. Cerium, on the other hand, acts both as a triad and a tetrad.

Tin possesses some properties common to the previously mentioned elements of this series. Thus it forms a volatile tetrachloride and a dioxide capable of combining with oxides of metals to form stannates (e.g. Na_2SnO_3). But in its dyad capacity it has perhaps more resemblance to copper than to any other element. Lead also acts as a dyad and as a tetrad. The dyad salts are stable, and well known; the tetrad salts are few in number and are easily decomposed by heat. In the insolubility of its chloride it presents some analogy with silver, mercury, and thallium; and its sulphate, like those of calcium, strontium, and barium, is insoluble. Thorium is a very rare element which appears to resemble titanium and zirconium. So far as is known, it acts solely as a tetrad.

§ 96. The fifth series presents us with material for similar remarks. The first member, nitrogen, resembles phosphorus, both in its compounds with oxygen, and in the compounds of its oxides with those of the metals, and also in its compound with hydrogen. Yet the difference in the behaviour of these elements is no less striking. Nitrogen has little tendency to combine with other elements, while phosphorus in a high degree, and the remaining members of the group, in less degree, combine readily. Although the elements of this series act for the most part as triads, yet all of them also probably function as pentads, and nitrogen and vanadium are characterised by their varied valency. The acid character of the oxides is most marked in the earlier members of the series; while the later ones display more marked basic properties. The most striking series is arsenic, antimony, and bismuth; a marked resemblance exists between these elements, as well as among their compounds.

In the sixth series, the element oxygen stands alone, manifesting only some analogy with sulphur, more indeed in the formulae of its compounds than in their properties. Sulphur, selenium, and tellurium form a very well marked group. These four elements each unite with two atoms of hydrogen, forming in the case of oxygen, water, and in the case of sulphur, selenium, and tellurium, gases which resemble each other closely. The chlorides of oxygen, however, differ materially from those of sulphur, selenium and tellurium. Chromium, molybdenum, tungsten, and uranium, in their oxides, of the formula RO_3, and in the salts of this oxide exhibit analogy. But chromium itself is more similar to aluminium, and to iron in the ferric state, than to any other elements.

§ 97. In the seventh series as in the sixth, a close resemblance is noticeable between the second, fourth, and sixth members. Fluorine, like oxygen, presents marked differences. Thus silver fluoride is soluble, while silver chloride, bromide, and iodide are insoluble in water. Yet hydrogen fluoride has marked analogy with the corresponding chloride, bromide and iodide. So far as is known, fluorine is a gas, and in this it resembles oxygen. But the boiling-point of hydrogen fluoride is higher than those of hydrogen chloride, bromide, and iodide, just as the boiling-point of water is above those of hydrogen sulphide, selenide, and telluride. Fluoride of calcium is insoluble in water, while the corresponding chloride, bromide and iodide are among the most soluble salts known. These and similar facts show the dissimilarity between fluorine and the *halogens*, as chlorine, bromine and iodine are termed. On the other hand there is a most striking similarity between the halogens themselves as well as between their compounds, and the resemblance is even closer than that between sulphur, selenium, and tellurium.

Manganese, the only other known member of this series, has, like chromium in the previous series, more resemblance to iron than to any other element. The likeness to other members of its series is slight. It forms permanganates of the general formula $R_2{}^{I}Mn_2O_8$, which have the same crystalline form, or are *isomorphous* with the perchlorates $R_2{}^{II}Cl_2O_8$. But besides this, it is difficult to point to any resemblance. The element manganese is a metal resembling iron in appearance and properties, while chlorine is a yellowish green gas or liquid; bromine, a red gas or liquid, and iodine a violet gas, or a blue-black solid. The salts of manganese also resemble those of iron.

§ **98.** The eighth series consists of nine elements arranged in three sets of three; and the members of each set bear a close resemblance to each other. The first set contains iron, nickel, and cobalt. These metals act both as dyads and as triads. The dyad character is well marked in all; but the triad character is most pronounced in iron; triad compounds of nickel and cobalt are more unstable than those of iron. The rare metals, ruthenium, rhodium, and palladium are found associated. All of these have high melting-points, and present a similar appearance. They act both as dyads and tetrads, and some compounds are known in which they act as triads and hexads. Similar characters are presented by the metals of the next set, iridium, platinum and osmium, all of which melt at extremely high temperatures. Yet there is considerable difference in the behaviour of the individual members of this set. Iridium and platinum do not directly unite with oxygen; but osmium easily combines, forming OsO_4. The dyad and tetrad compounds of platinum are best marked; iridium forms triad compounds, while osmium acts as a dyad, tetrad, and octad.

§ 99. It will have been noticed that in the table given in § 93, numerous gaps occur. Since Newlands first drew attention to this arrangement of the elements, several elements have been discovered, and several gaps have been filled. Mendelejeff, indeed, predicted with tolerable accuracy in 1871 the properties of two elements, at the time undiscovered, to which he gave the provisional names eka-boron and eka-aluminium. Lecoq de Boisbaudran, in 1876, discovered the element gallium in zinc ores, and it was found to possess the atomic weight 68·8, instead of the one surmised by Mendelejeff, 68. And eka-boron was identified with scandium discovered by Cleve and Nilson in 1879. It can hardly therefore be doubted that the discovery of other elements will fill up the gaps in the foregoing table.

The arrangement shown has, however, not merely pointed to the probable existence of undiscovered elements, but it has been instrumental in assigning the correct atomic weight to several elements of which the atomic weight was doubtful. Thus before Newlands had suggested the table, it was doubtful whether the atomic weight of indium was 75·6 or 113·4. In the first case its atomic weight is twice its equivalent, 37·8, and its oxide would possess the formula InO; but in the second case, indium is a triad, its atomic weight three times its equivalent, and its oxide, In_2O_3. In the first case indium would occupy a place between arsenic and selenium, elements with which it has no analogy. But in the second, it falls in the cadmium group and in the gallium series, and with these elements it exhibits a fairly close analogy.

The atomic weight of uranium has been changed from 119·7 to 238·5 from similar considerations. There is still dispute concerning the correct atomic weight of beryllium; from certain analogies between beryllium and aluminium, Berzelius classed beryllium as a triad; its atomic weight 13·65 would therefore be three times its equivalent, 4·55. It would therefore occupy a position between carbon and nitrogen; but not only is there no gap for an element in that position, but beryllium has not the remotest relation either to carbon or nitrogen, for it possesses very different properties from these elements. Determinations of the specific heat of beryllium have given in the hands of different experimenters the most varied results, partly owing to the fact that the specific heat of elements of low atomic weight is sometimes abnormal, and partly owing to the difficulty of obtaining metallic beryllium in a pure state. The balance of evidence, however, goes to prove, what is evident from a consideration of the periodic table, that beryllium is a dyad, with the atomic weight 9·1.

§ **100.** The atomic weights given in the periodic table have been determined by many experimenters, and with varying accuracy; the numbers given are deduced from the means of the best results. Many of them, however, are only approximately correct, and new determinations will correct the numbers given, possibly altering some of them by more than a unit. A conjecture was thrown out, long ago, by Prout, that the atomic weights were all multiples of that of hydrogen. If the elements which possess an atomic weight consisting of whole numbers, and those which differ from whole numbers by less than one-tenth of a unit be counted, it will be found that they number nearly 20, out of a total of 67. The exact atomic weight of many of the others is a matter of doubt, and it may be found that many more have atomic weights approximating to whole numbers. But on the other hand, determinations of the most exact nature, for instance of the atomic weights of silver, chlorine, and iodine, point to a different conclusion.

Although this periodic table has connected many elements which exhibit great analogy with each other in a systematic manner, yet it brings elements into the same groups and series which do not exhibit any very striking analogy, as has been already shown. Indeed many elements are removed from what would be supposed to be their natural positions. Nevertheless such a classification, even if a provisional one, tends to throw light on their analogies with one another, and to pave the way for further discovery.

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